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# Advances in porous organic polymers: syntheses, structures, and diverse applications

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Porous organic polymers (POPs) are organic macromolecules that are considered emerging materials because of their high specific surface areas, tunable porosities, low densities, high chemical and thermal stabilities, variable compositions, convenient post-functionalization, extended  $\pi$ -conjugations, and their high contents of carbon, nitrogen, oxygen, and other non-metallic atoms. POPs have been classified into four types: covalent triazine frameworks (CTFs), hypercrosslinked polymers (HCPs), covalent organic frameworks (COFs), and conjugated microporous polymers (CMPs). These materials have potential applications in, for example, gas capture/separation, energy storage, H<sub>2</sub> production from water, photocatalysis, chemical sensing, perovskite solar cells, water treatment, optical devices, and biomedicine. In this review, we provide an overview of recent reports describing the preparation and various applications of POPs.

## 1. Introduction

Porous structures have existed in nature for a very long time in, for example, charcoal, biological tissues, and rocks.<sup>1</sup> The word “porous” is usually used to describe a material featuring interconnected permanent voids that allow the passage of gases or liquids.<sup>1</sup> Porous materials are applied in many technological and scientific fields, with a huge number of new advanced porous materials having been developed during the last two decades.<sup>2–14</sup> Based on the IUPAC classification, porous materials can be divided, based on their pore diameters, into microporous (<2 nm), mesoporous (>2 nm and <50 nm), and macroporous (>50 nm) materials.<sup>15–22</sup> Various porous materials have been constructed from metal–organic frameworks (MOFs) and porous organic polymers (POPs).<sup>1,23–28</sup> MOFs are typically crystalline porous materials or porous coordination polymers obtained through the formation of coordinate bonds between organic ligands and clusters or metal ions to form voids within the framework structure, thereby resulting in porosity.<sup>23–25</sup> In the past two decades, many groups have prepared various subclasses of POP frameworks, including porous aromatic frameworks (PAFs), covalent triazine frameworks (CTFs), covalent organic frameworks (COFs), polymers of intrinsic microporosity (PIMs), hypercrosslinked

polymers (HCPs), and conjugated microporous polymers (CMPs) (Fig. 1).<sup>1,29–33</sup> The preparation of each kind of POP generally occurs through network reactions.<sup>1</sup> All POPs are amorphous materials—except for a small number of CTFs and COFs that are crystalline materials with ordered structures prepared under thermodynamic control.<sup>1</sup> Like nanoporous materials, POPs have many potential applications because of their high surface areas and uniform pore sizes, with large numbers of channels and active sites available for chemical reactions.<sup>3,34–37</sup> Accordingly, POPs have attracted attention for their use in, for example, the degradation of organic pollutants, energy storage, photocatalysis, H<sub>2</sub> evolution, light harvesting, photovoltaics, luminescence, gas adsorption and separation, chemical sensing, and drug loading and delivery.<sup>38–54</sup> Various morphologies of POPs, including nanotubes, nanospheres, and nanosheets, can be controlled by varying the synthetic method, the monomer structure, or the reaction conditions.<sup>45,48,55</sup> Furthermore, the surface areas of POPs, typically in the range 100–1000 m<sup>2</sup> g<sup>−1</sup>, are higher than those of MOFs and porous carbons.<sup>3</sup> In 2007, Yaghi *et al.* prepared a 3D-COF-103 possessing a high Brunauer–Emmett–Teller (BET) surface area of 4210 m<sup>2</sup> g<sup>−1</sup>.<sup>56</sup> Ben *et al.* used the Yamamoto reaction to prepare a PAF (PAF-1) exhibiting a high specific area (4210 m<sup>2</sup> g<sup>−1</sup>).<sup>57</sup> The insolubility of POPs in organic solvents, due to their rigid chemical bonds and high degrees of polymerization, can simplify the separation and recycling of POPs.<sup>3</sup> In this review, we provide an overview of recent reports describing the preparation of POPs (including CTFs, COFs, HCPs, and CMPs) and their applications in photocatalytic water splitting for H<sub>2</sub> evolution, gas capture and separation, chemosensing, the removal of dyes and metals, organic synthesis, and energy storage.

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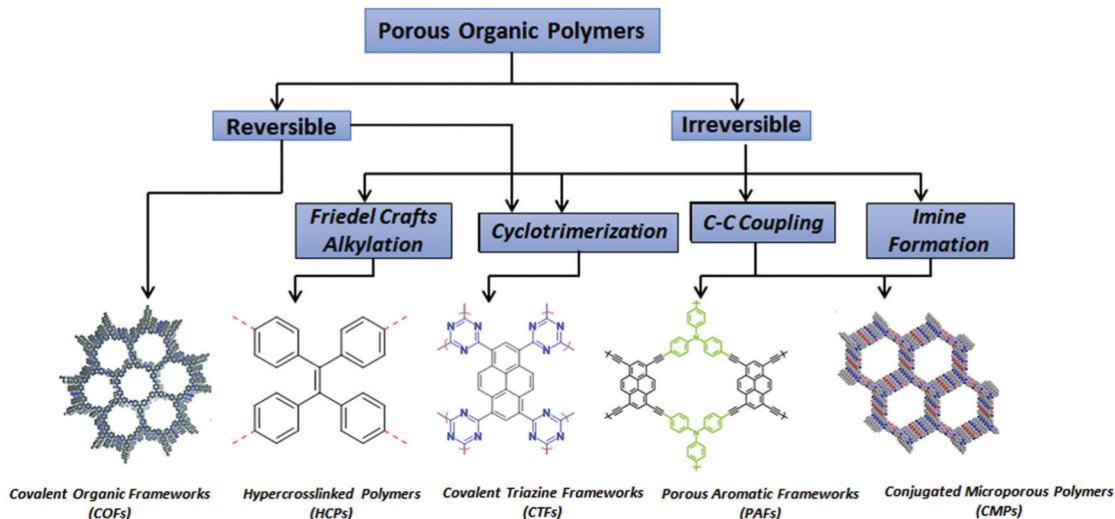


Fig. 1 Types of porous organic polymer frameworks and their coupling formation reactions.

## 2. Preparation of POPs

In this section, we discuss progress in the synthetic methodologies that are widely used for the preparation four kinds of POPs: HCPs, CTFs, CMPs, and COFs.

### 2.1. Preparation of HCPs

HCPs are porous polymers that have attracted much attention for their extended conjugation; tunable porosities; high surface areas; high mechanical, chemical, and hydrothermal stabilities; variety of potential synthetic methods; and facile post-functionalization after HCP formation.<sup>58–63</sup> Many methods have been used to determine the chemical structures, thermal stabilities, morphologies, and textural characteristics (*e.g.*, pore size diameters and surface areas) of HCPs, including Fourier transform infrared (FTIR) spectroscopy, elemental analysis, solid state nuclear magnetic resonance (NMR) spectroscopy, transmission electron microscopy (TEM), optical microscopy, field emission scanning electron microscopy (SEM), N<sub>2</sub> adsorption isotherms, and thermogravimetric analysis (TGA).<sup>58–63</sup> Davankov and Tsyurupa were the first to generate three-dimensional (3D) network structures of linear polystyrene (PS) with high surface areas (up to 2000 m<sup>2</sup> g<sup>-1</sup>) as the first HCP material, through post-crosslinking of a PS precursor in the swollen state.<sup>64</sup> The formation HCPs can be achieved through acid-catalyzed Friedel–Crafts reactions involving a Lewis acid catalyst, a reaction solvent, and arene-based nucleophilic and electrophilic species.<sup>65</sup> To avoid products forming through side reactions during the knitting step, the reactions are performed under Ar and N<sub>2</sub> atmospheres to afford pure HCPs as solid materials.<sup>65</sup> The incorporation of metal species into HCPs can be performed through post-modification—by introducing a metal salt or complex—or by using a metal complex as a comonomer or monomer during the knitting reaction (Fig. 2).<sup>65</sup> HCP materials have been employed in many applications, including energy storage; (supercapacitor devices, and lithium, sodium, and potassium batteries); chemical sensing; heterogeneous

catalysis; optoelectronic devices; drug delivery; gas capture and separation; and chromatographic separation.<sup>58–65</sup>

### 2.2. Preparation of CTFs

CTFs are partially crystalline, amorphous porous materials possessing conjugated and layered structures.<sup>66</sup> Thomas and co-workers were the first to report examples of CTF materials containing aromatic rings and triazine moieties in the core.<sup>6</sup> CTFs have attracted much attention for their potential applications in, for example, CO<sub>2</sub> reduction, pollutant degradation, organosynthesis, water splitting, H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub> production, and organic semiconductor devices.<sup>67–72</sup> Several approaches have been used for the preparation of CTFs, including cyclotrimerization of nitrile groups through direct or indirect methods in the presence of molten ZnCl<sub>2</sub> at 400 °C; superacid-catalyzed trimerization; Suzuki cross-coupling; Ni-catalyzed Yamamoto coupling; and P<sub>2</sub>O<sub>5</sub> catalysis at 400 °C (Fig. 3).<sup>66</sup> The preparation of CTFs with highly crystalline structures requires the selection of monomers with planar characteristics; the use of nonplanar monomers leads to the formation amorphous or semicrystalline CTFs.<sup>73–76</sup> To date, only a few crystalline CTFs have been reported. For example, Tang *et al.* found that the degree of crystallinity of CTFs and the formation of uniform layered structures increased upon increasing the microwave power from 20 to 100 W.<sup>77</sup> Interestingly, Xu *et al.* prepared a two-dimensional (2D) CTF with a well stacked structure within 10 min at 25 °C through a TfOH-catalyzed interfacial reaction, with simple purification procedures applied after the trimerization reactions (Fig. 4).<sup>78</sup> They found that the crystalline CTFs formed using this approach were AB-staggered; in contrast, mostly crystalline CTFs exhibiting the AA stacking mode were obtained when using the ionothermal method.

### 2.3. Preparation of CMPs

CMPs are microporous organic polymers that are emerging materials because of their permanent building blocks; huge



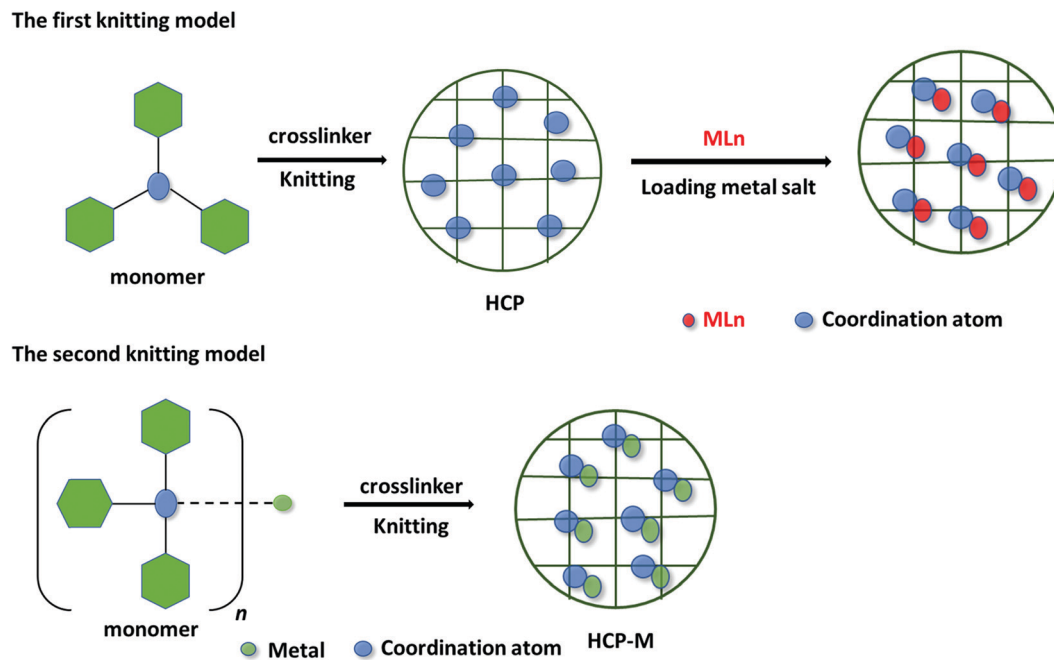


Fig. 2 Schematic cartoon for incorporating metal species into HCP frameworks via two different knitting models. Reproduced from ref. 65 with permission from Wiley-VCH.

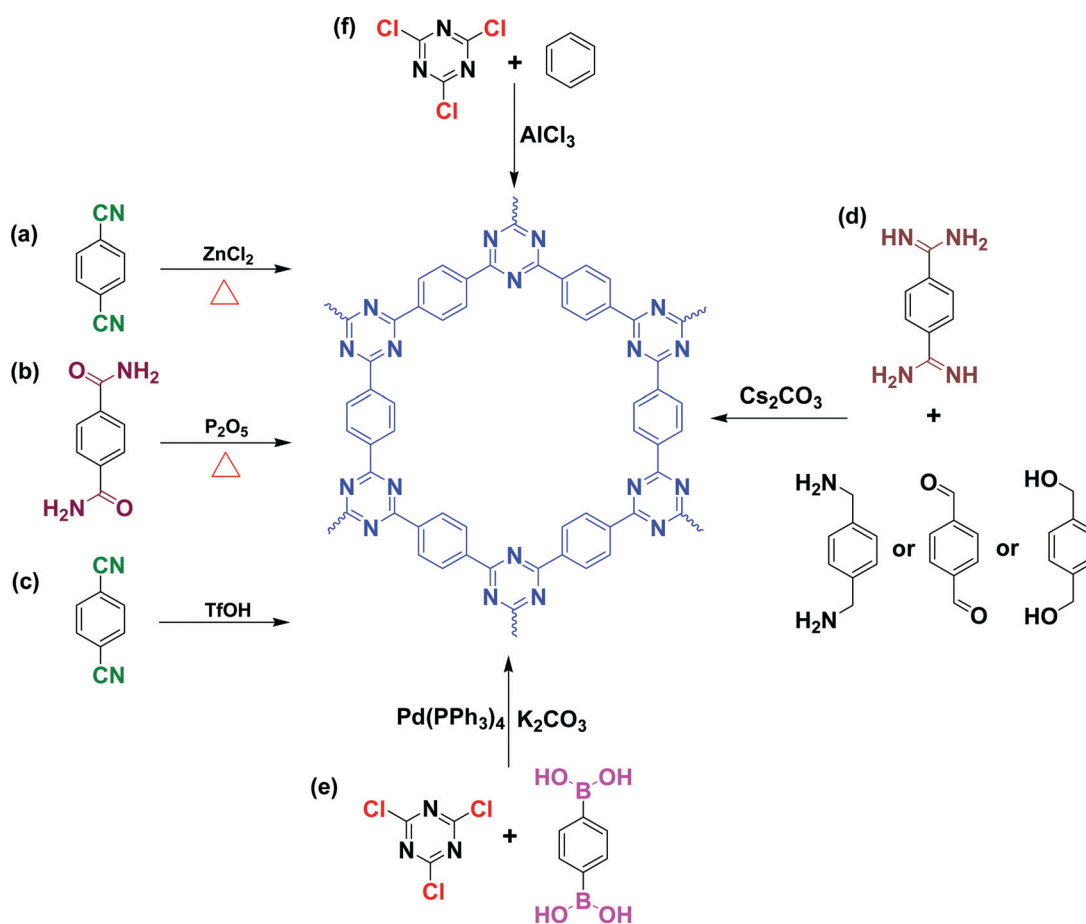


Fig. 3 Formation of CTFs via direct or indirect approaches. Reproduced from ref. 66 with permission from American Chemical Society.



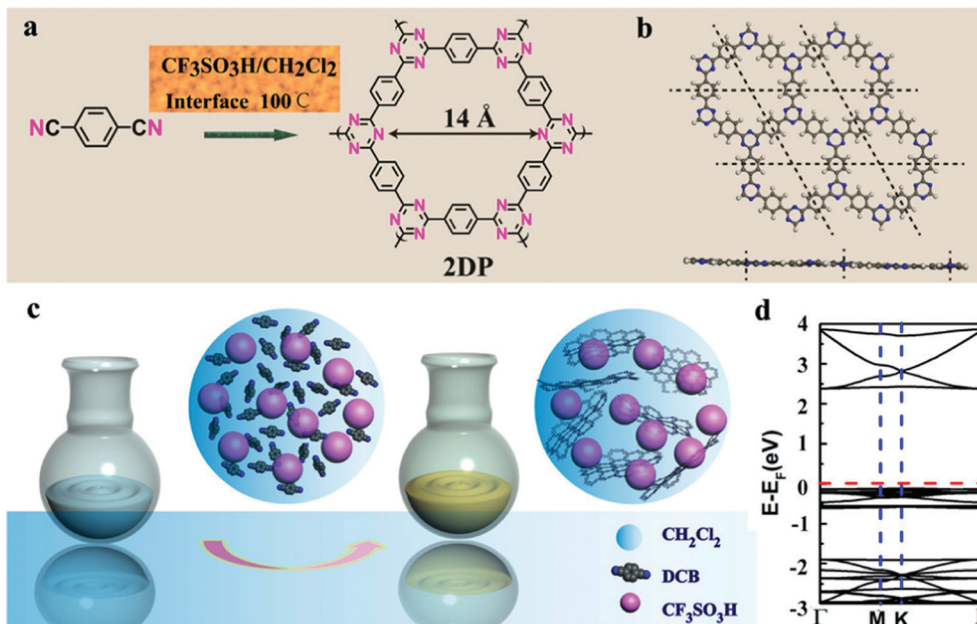


Fig. 4 (a) and (b) Synthesis of 2D-CTFs through polymerization at  $\text{CH}_2\text{Cl}_2/\text{CF}_3\text{SO}_3\text{H}$  interfaces, (b) and (d) represent the atomic structure and DFT band structure of the 2D-CTF. Reproduced from ref. 78 with permission from American Chemical Society.

surface areas; structural adjustability, diversity, and modularity; expanded degrees of conjugation; and excellent physicochemical stabilities.<sup>79–82</sup> Accordingly, CMPs have been used widely as materials for photovoltaic devices, light-harvesting, photocatalysis, adsorbents, luminescent materials, and clean energy applications (e.g., supercapacitors,  $\text{H}_2$  storage, photocatalytic cells, metal-ion rechargeable batteries,  $\text{CO}_2$  capture and conversion, and fuel cells).<sup>79–82</sup> The interesting properties of CMPs arise from (i) their expanded conjugated structures along the polymer chains (significantly enhancing their chemical and physicochemical stabilities) and (ii) their high surface areas and highly crosslinked polymeric network structures (improving their electrochemical activities, cycle stabilities, and kinetics and preventing the active material from dissolution into organic electrolytes).<sup>79–84</sup> The approaches used most widely for the preparation of CMPs include phenazine ring fusion, electropolymerization, alkyne metathesis, Schiff base formation, and Yamamoto, Heck, Sonogashira–Hagihara, Buchwald–Hartwig, and Suzuki–Miyaura cross-couplings. These methods allow good selectivities, a range of different of substrates, suitable reaction conditions, simple post-synthetic modifications, and the high-yield production of CMPs with high specific surface areas.

#### 2.4. Preparation of COFs

COFs are important emerging materials with potential applications in a wide range of fields, including optics, gas capture, lithium–sulfur batteries, electrocatalysis, metal adsorption, light harvesting, and sensing; they are easy to prepare with high surface areas and total pore volumes, moderate physical and chemical properties, and homogeneous micropores.<sup>85–92</sup> COFs have been formed with 2D and 3D network structures comprising backbones containing carbon (C) and hydrogen (H) atoms as well as other

elements, including oxygen (O), boron (B), sulfur (S), and nitrogen (N) atoms. Various topologies of 2D and 3D COFs can be induced by varying the geometries and dimensions of their building blocks (Fig. 5).<sup>93</sup> Compared with other porous polymeric materials, the ability to predict the skeleton structures of COFs is unique. The many synthetic techniques available for the preparation of COFs include sonochemical methods, interfacial synthesis, ionothermal synthesis, mechanochemical methods, microwave-assisted synthesis, and solvothermal synthesis.<sup>93</sup> The fabrication of COF skeletons with particular pore sizes and symmetries depends on the choice of suitable linkers and organic building blocks. The types of linkers that have been used for the preparation of COFs include hydrazone, phenazine, imine, azine, boroxine, imide, and triazine units (Fig. 6).<sup>93</sup> 2D COF frameworks can have nine different topologies: hexagonal layer (hxl), kgd, tth, mtf, bex, kagome (kgm), hexagonal tungsten bronze (htb), square lattice (sql), and hcb (Fig. 7).<sup>94</sup> Feng and co-workers prepared a 3D anionic CD-COF (rra net) containing trinodal secondary building units through the condensation reaction of  $\gamma$ -CD with  $\text{B}(\text{OMe})_3$  in the presence of LiOH under microwave conditions.<sup>95</sup> In addition, Yaghi *et al.* obtained a COF-based tth topology when combining square-planar, hexagonal, and triangular building blocks and observed tth topology tiling.<sup>96</sup>

## 3. Potential applications of POPs

### 3.1. $\text{CO}_2$ capture

POPs are ideal candidates for capturing  $\text{CO}_2$  gas in a green and environmentally friendly manner. Very recently, the Tan group prepared two novel inorganic–organic crosslinked polymers (HCP-PN-1, and HCP-PN-2) based on phosphazene moieties through Friedel–Crafts alkylations for the nucleophilic





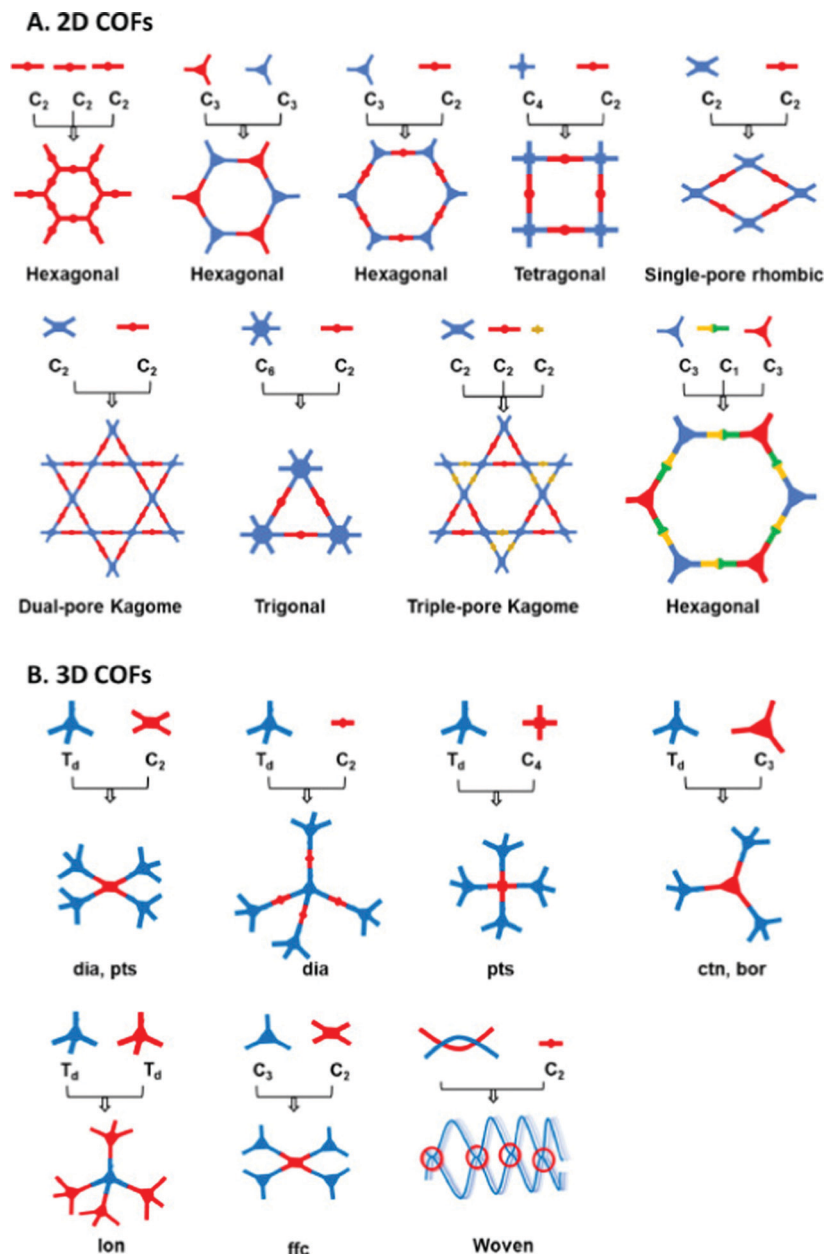


Fig. 5 Topology diagrams representing a general basis for COF design and the construction of (A) 2D COFs and (B) 3D COFs.<sup>93</sup> Reproduced from ref. 93 with permission from Elsevier.

substitution of hexachlorotriphosphazene with 2-naphthol (PN-Nap-1 and PN-Nap-2) to give nitrogen- and phosphorus-enriched HCPs (Fig. 8).<sup>97</sup> Interestingly, these HCPs had hierarchical pore structures and high surface areas (based on BET measurements) that led to high degrees of CO<sub>2</sub> adsorption (HCP-PN-1: 72 mg g<sup>-1</sup>; HCP-PN-2: 57 mg g<sup>-1</sup>; at 273 K). Li *et al.* prepared MOP-PZ containing N=C and NH groups through a Scholl reaction of 3,5-diphenyl-1*H*-pyrazole in the presence of AlCl<sub>3</sub> in CHCl<sub>3</sub> as the solvent. They prepared the hybrid material MOP-PZ-Ag by embedding silver nanoparticles (NPs) into MOP-PZ, and found that MOP-PZ-Ag functioned as a heterogeneous catalyst for the production of propionic acid through the carboxylation of some terminal alkynes; this stable

hybrid material also displayed an excellent degree of CO<sub>2</sub> adsorption (183.7 mg g<sup>-1</sup>).<sup>98</sup> Wang and co-workers prepared nitrogen-enriched microporous polymers containing various contents of amino groups through condensation reactions of melamine with formohydrazide, formamide, *N,N*-dimethylformamide (DMF), and *N*-methylformamide. These four polymers possessed pore diameters of 0.52–1.10 nm and specific surface areas of 612–748 m<sup>2</sup> g<sup>-1</sup>, with the BET method, and SEM, and TEM analysis revealing that they were agglomerates of tiny particles with an irregular shape and porous structures; the four polymers provided CO<sub>2</sub> uptakes of up to 103 mg g<sup>-1</sup> at 273 K.<sup>99</sup> Liang *et al.* prepared four kinds of CMPs and used a post-knitting approach to improve their porosities, affording



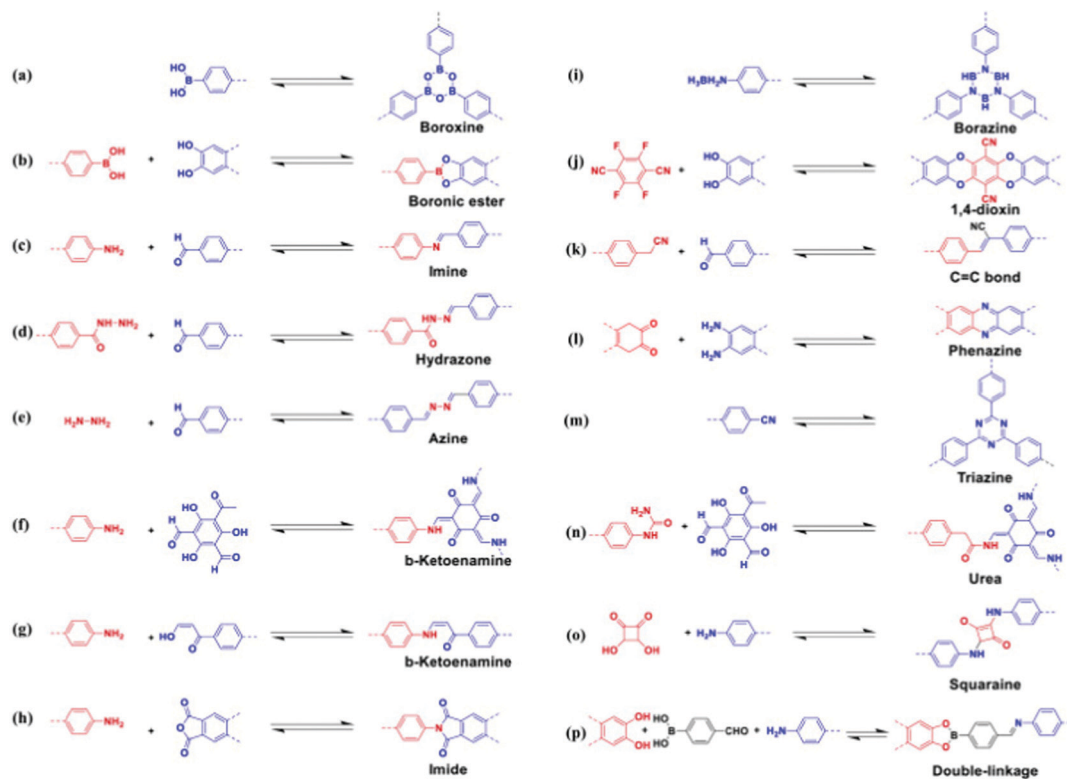


Fig. 6 Various linkages for COF formation. Reproduced from ref. 93 with permission from Elsevier.

eight CMP-based HCPs (KCMPs) (Fig. 9).<sup>100</sup> These KCMPs had high specific surface areas (up to  $2267 \text{ m}^2 \text{ g}^{-1}$ ), high pore volumes (up to  $3.27 \text{ cm}^3 \text{ g}^{-1}$ ), and excellent degrees of  $\text{CO}_2$  uptake (up to  $175.12 \text{ mg g}^{-1}$  at 273 K). Das *et al.* prepared two kinds of CTFs based on 1,2,3-triazolo units; their Tz-CTF polymeric frameworks exhibited excellent  $\text{CO}_2$  uptake capacities, with a high surface area, chemical and thermal stabilities, agglomerated tiny particles, and regular porous structures, based on SEM and TEM imaging.<sup>101</sup> Our group also prepared two bicarbazole-based COFs (Cz-BD, and Cz-DHBD) through Schiff-base condensations of Cz-4CHO (as the  $C_2$ -symmetric knot) with BD and DHBD.<sup>102</sup> These Cz-BD and Cz-DHBD COFs possessed high surface areas (up to 2111 and  $992.2 \text{ m}^2 \text{ g}^{-1}$ , respectively) as well as thermal stability up to 507 °C. The Cz-DHBD COF featured a kagome structure, due to intramolecular  $\text{OH} \cdots \text{N}$  hydrogen bonding, that increased the steric bulk hindrance and decreased the nucleophilicity of the imino nitrogen atoms, thereby decreasing its ability to capture  $\text{CO}_2$  ( $110.59 \text{ mg g}^{-1}$ ) relative to that of the Cz-BD COF ( $125.95 \text{ mg g}^{-1}$ ). In addition, we have prepared hollow microspherical and microtubular carbazole-based COFs through condensations of Car-3 $\text{NH}_2$  and the trimethyl linkers TPA-3CHO, TPP-3CHO, and TPT-3CHO with various degrees of planarity, obtaining high surface areas of 1334, 743, and  $721 \text{ m}^2 \text{ g}^{-1}$ , respectively. Due to their high surface areas, these Car-TPA, Car-TPT, and Car-TPP COFs provided high degrees of  $\text{CO}_2$  capture, with recorded uptake rates of up to 61, 42, and  $34 \text{ mg g}^{-1}$ , respectively, at 298 K. Although Car-TPT and Car-TPP had similar surface areas, the former provided a higher

$\text{CO}_2$  capture rate because of the higher nitrogen content of the triazine units in the Car-TPT COF.<sup>103</sup> The effect of the nitrogen content on the  $\text{CO}_2$  capture ability of COFs was also observed in six 2D COFs displaying various planarities, symmetries, and nitrogen contents, synthesized through the condensation reaction of TPA-3 $\text{NH}_2$  and TPT-3 $\text{NH}_2$  (as triarylamine monomers) with the monomers TPA-3CHO, TPP-3CHO, and 2TPT-3CHO (with various degrees of planarity) (Fig. 10).<sup>104</sup> Here, TPT-3 $\text{NH}_2$  is more planar than TPA-3 $\text{NH}_2$ , and TPT-3CHO is more planar than TPP-3CHO and TPA-3CHO. The COFs with lower planarity possessed lower surface areas; those with higher nitrogen contents and higher nucleophilicities displayed higher degrees of  $\text{CO}_2$  capture. As expected, the higher nitrogen contents in the TPT-based COFs provided higher rates of  $\text{CO}_2$  capture (up to  $92.38 \text{ mg g}^{-1}$  at 273 K for TPT-COF-6), with the greater planarity of their building blocks also enhancing the morphology to favor  $\text{CO}_2$  capture.<sup>104</sup> We have also prepared  $\beta$ -ketoenamine-linked COFs (TFP-TPA, TFP-Car, and TFP-TPP) through solvothermal Schiff-base [3+3] polycondensations of TFP-3OHCHO with three tris(aminophenyl)-presenting derivatives (possessing amino, carbazole, and pyridine units, respectively).<sup>105</sup> The TFP-TPA, TFP-Car, and TFP-TPP COFs possessed different degrees of planarity and surface areas of 457, 362, and  $686 \text{ m}^2 \text{ g}^{-1}$ , respectively. The higher degrees of planarity of the TFP-Car and TFP-TPP COFs resulted in higher thermal stabilities and stronger interactions with  $\text{CO}_2$  molecules at 273 K (up to 190 and  $200 \text{ mg g}^{-1}$ , respectively) relative to those exhibited by the lower-planarity TPA-Car COF ( $183 \text{ mg g}^{-1}$ ).<sup>105</sup> Nagai *et al.* reported four



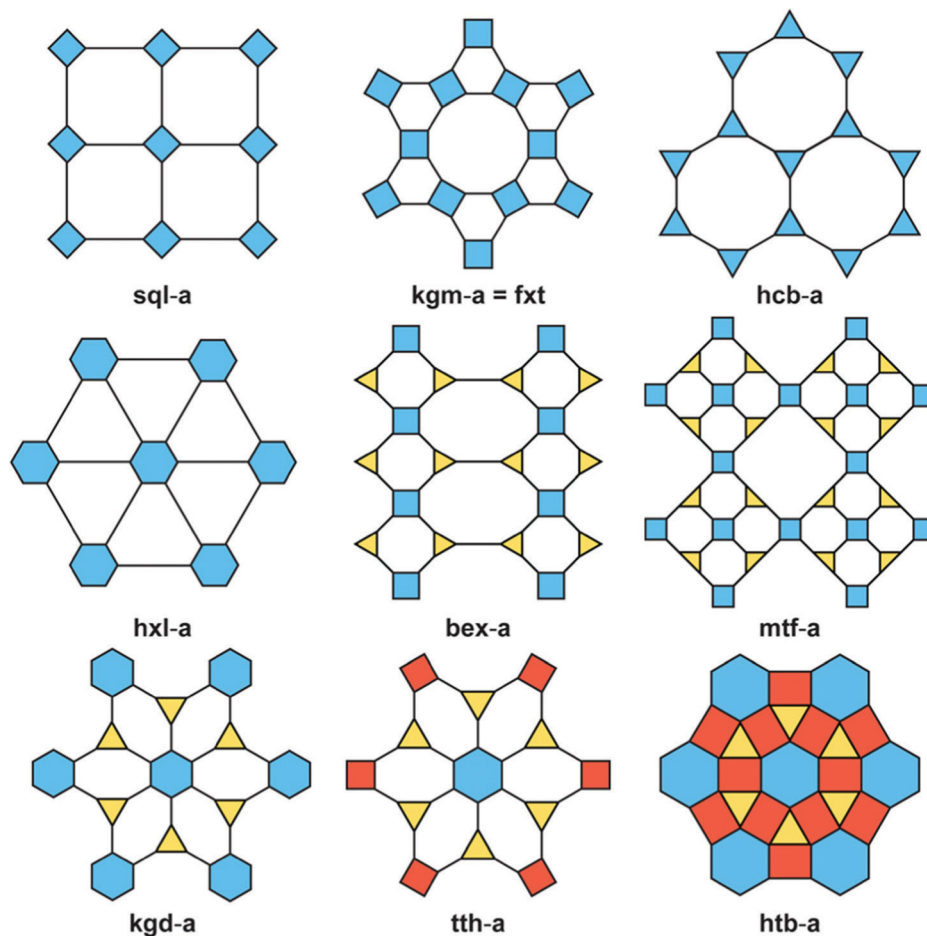


Fig. 7 Various topologies in 2D COFs. Reproduced from ref. 94 with permission from American Chemical Society.

types of PI-COF prepared through solvothermal reactions of TAPA and TAPB with PMDA and NTCDA (Fig. 11).<sup>106</sup> These PI-COF materials had specific surface areas exceeding  $500 \text{ m}^2 \text{ g}^{-1}$  and were applied for  $\text{CO}_2$  uptake. We have used Schiff base formation, reduction, and Mannich and Sonogashira-Hagihara couplings to prepare two new CMPs (TPE-TPE-BZ, and Py-TPE-BZ) featuring benzoxazine-linked tetraphenylethylene and pyrene units (Fig. 12)<sup>107</sup> Upon thermal treatment, the benzoxazine units in the backbones of the TPE-TPE-BZ and Py-TPE-BZ CMPs underwent ring opening polymerizations to form new materials displaying high performance for  $\text{CO}_2$  uptake, due to the presence of phenolic OH and Mannich bridges capable of hydrogen bonding with  $\text{CO}_2$  molecules.

### 3.2. Dyes and iodine adsorption

Yu *et al.* prepared four HCP materials (BCB, Py, CCBCB, and CCPy-CMP) based on perylene, bicarbazole, and triazine units (Fig. 13).<sup>108</sup> According to BET analyses, the surface areas of BCB, Py, CCBCB and CCPy-CMP were 545, 624, 220, and  $20 \text{ m}^2 \text{ g}^{-1}$ , respectively; their surface morphologies featured nanotubes, graphitic flakes, aggregated particles, and nanosheet stacks, respectively. The  $\text{I}_2$  uptake of the CCBCP-CMP sample [ $11.56 \text{ wt} (\text{m}^{-2} \text{ g}^{-1})$ ] was higher than those of the other precursors

because of its high surface area and high content of N-heteroatoms. Recently, we used Friedel-Crafts polymerization to prepare the hybrid inorganic/organic porous materials POSS-TPE and POSS-TPP based on cubic octavinylsilsequioxane (OVS) and tetraphenylethylene and tetraphenylpyrazine units, respectively. The as-prepared POSS-TPE had a high surface area ( $741 \text{ m}^2 \text{ g}^{-1}$ ) and good thermal stability, as determined using  $\text{N}_2$  adsorption/desorption and TGA, respectively.<sup>109</sup> The Alameddine group prepared five CMP materials through Cu-catalyzed [4+2] benzannulations of 2,5-bis(phenylethynyl)tetraphthaldehyde with a series of 1,4-diarylethynyltritycene derivatives.<sup>110</sup> The resultant CMPs 1–5 were microporous, with high BET surface areas ( $794 \text{ m}^2 \text{ g}^{-1}$ ) and pore volumes ( $0.63 \text{ cm}^3 \text{ g}^{-1}$ ), and displayed good  $\text{I}_2$  uptake (166 wt%). Lin *et al.* constructed CTT-POP1, a POP containing triaryl triazine and featuring intramolecular hydrogen bonds, that functioned as an adsorbent for the dye methylene blue because of its surface wettability and capability for  $\pi$ - $\pi$  interactions.<sup>111</sup> The Das group prepared a series of covalent organic polymers (COPs) through the reactions of triptycene with derivatives of benzene-1,3,5-tricarboxaldehyde.<sup>112</sup> Interestingly, the surface areas of these resulting polymers were strongly affected by the number of OH groups in the I-COPs, as predicted from the BET profiles. Due to their high surface areas and uniform spherical shapes, determined



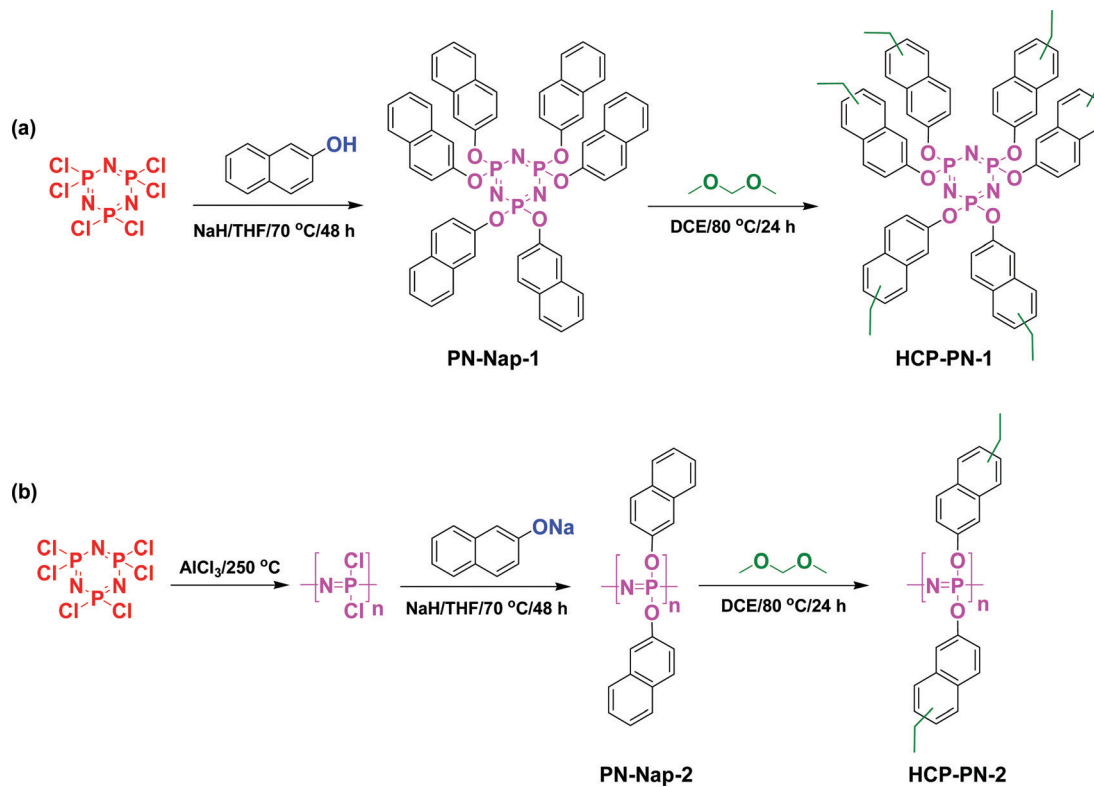


Fig. 8 Synthesis of (a) PN-Nap-2 and HCP-PN-2, (b) and (c)  $\text{CO}_2$  adsorption of PN-Nap-2 and HCP-PN-2 at 0 and 25 °C. Reproduced from ref. 97 with permission from American Chemical Society.

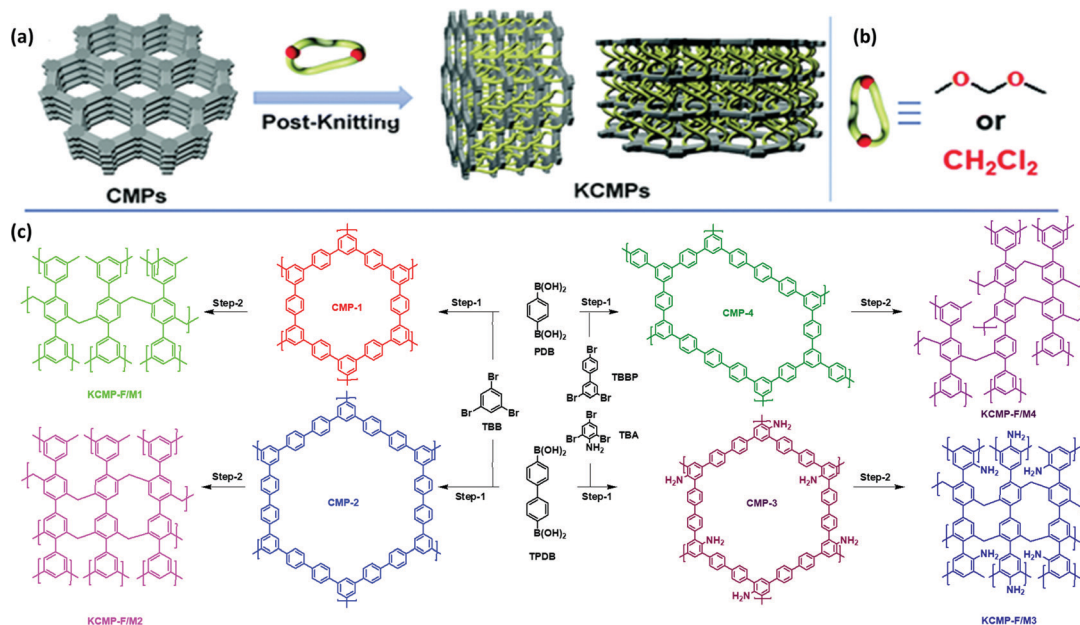


Fig. 9 Schematic cartoon for the synthesis of CMPs via the post-knitting method. (b) The cross-linker structure. (c) The synthetic routes for the KCMP via palladium-catalyzed Suzuki coupling and a Lewis acid catalyzed Friedel-Crafts reaction. Reproduced from ref. 100 with permission from the Royal Society of Chemistry.

from SEM images, the  $\text{I}_2$  capacities of these I-COPs were outstanding (*ca.* 4860  $\text{mg g}^{-1}$ ) when compared with those of other

COP materials. The ability to tune the charge density of COFs, when combined with their high crystallinities and high surface





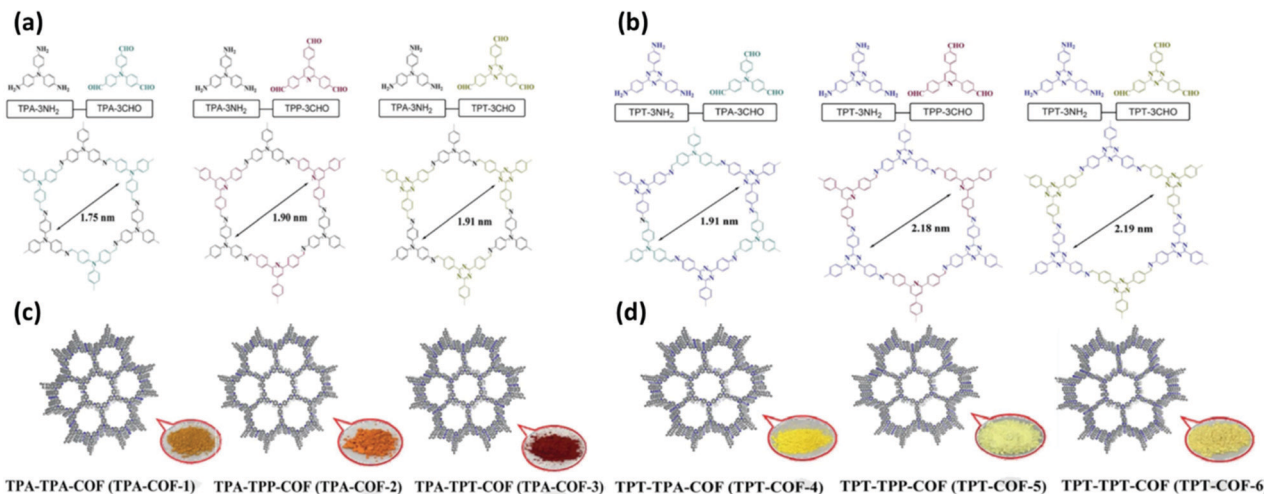


Fig. 10 (a and b) Synthesis of TPA-COF-1, TPA-COF-2, TPA-COF-3, TPT-COF-1, TPT-COF-2, and TPT-COF-3 through Schiff base reactions. (c and d) Their color photos. Reproduced from ref. 104 with permission from the Royal Society of Chemistry.

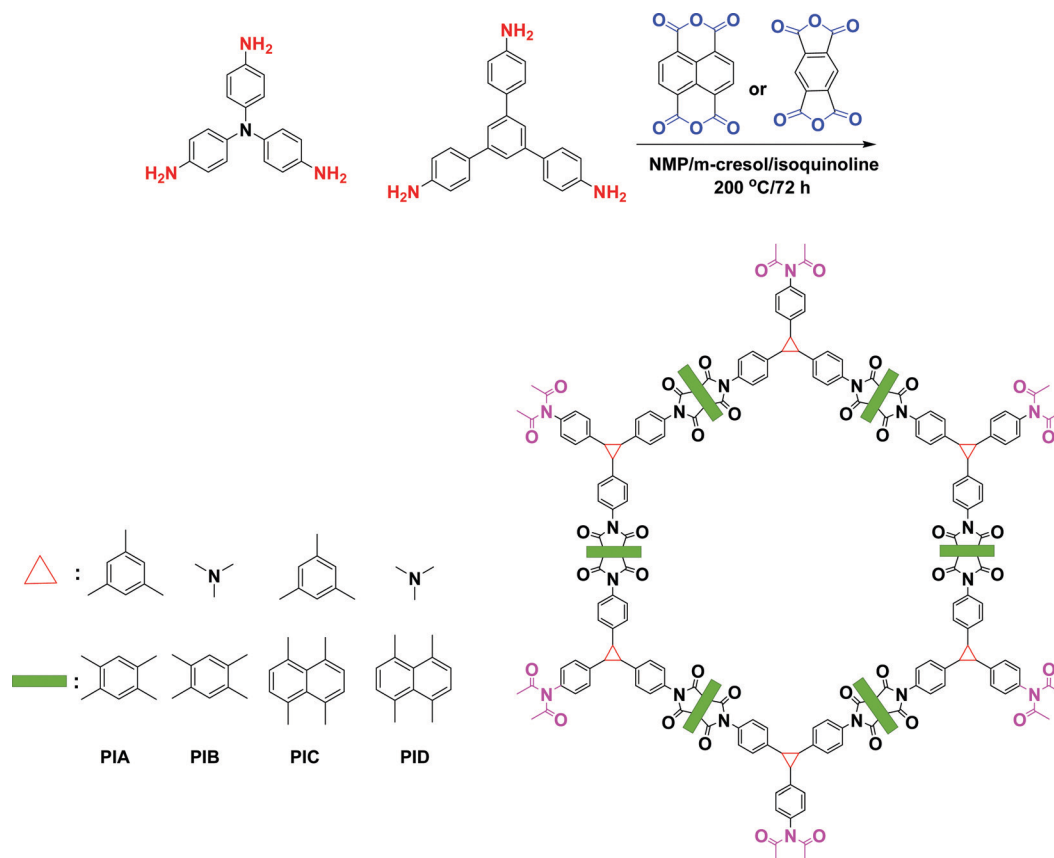


Fig. 11 Synthesis of the four polyimide COFs. Reproduced from ref. 106 with permission from American Chemical Society.

areas, makes them good candidates for capturing various chemicals, including dyes. Our group employed the previously mentioned BFTB-PyTA, BFTB-BFTB, and BFTB-BCTA COFs for dye adsorption; the adsorption efficacies of the hollow-structured BFTB-PyTA and BFTB-BFTB COFs were higher than that of the

non-hollow-structured BFTB-BCTA COF. These COFs displayed excellent adsorption performance (up to 99.2%) and confirmed that the controlling parameters of dye adsorption in the COFs were the surface area, the morphology, and the capability for  $\pi$ -stacking with the dye.<sup>113</sup>



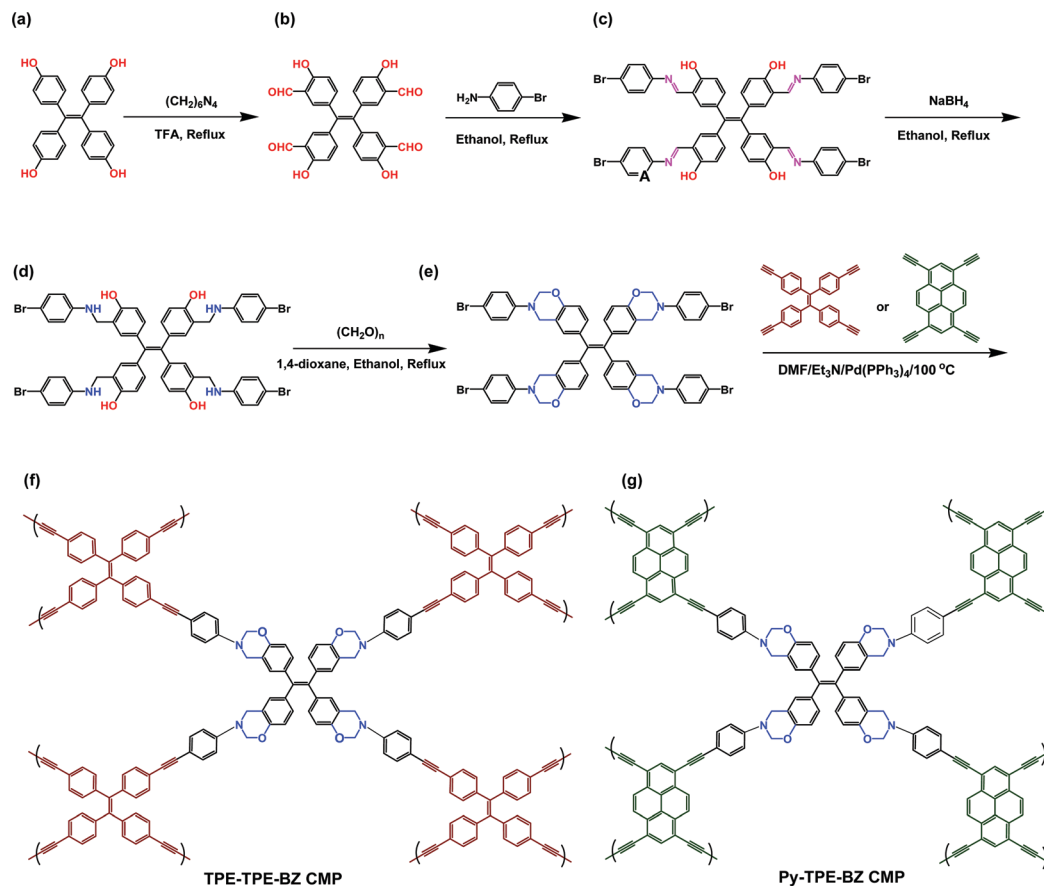


Fig. 12 Synthesis of the TPE-TPE-BZ CMP, and TPE-TPE-BZ CMPs through a multistep reaction. Reproduced from ref. 107 with permission from American Chemical Society.

### 3.3. Energy storage

There are many reports of the use of POPs as excellent materials for energy storage. For example, we have prepared microporous CTFs based on pyrene units (Pyrene-CTF-10, and Pyrene-CTF-20) through ionothermal reactions of 1,3,6,8-cyanopyrene (TCNPy) with different mole ratios of  $\text{ZnCl}_2$  at  $500^\circ\text{C}$ .<sup>114</sup> Pyrene-CTF-10 and Pyrene-CTF-20 possessed high surface areas ( $819$  and  $1019\text{ m}^2\text{ g}^{-1}$ , respectively) and capacitances ( $380$  and  $500\text{ F g}^{-1}$ , respectively). We have also prepared bicarbazole-based CTFs (Car-CTFs) based on Car-4CN. According to TGA and  $\text{N}_2$  adsorption/desorption analyses, our Car-CTFs had high specific surface areas (up to  $1400\text{ m}^2\text{ g}^{-1}$ ), and excellent coulombic efficiencies.<sup>115</sup> Mohamed *et al.* synthesized two HCPs (TPE-CPOP1, and TPE-CPOP2) based on tetraphenylethene as the main building unit and these obtained materials had high BET surface areas, amorphous structures, and high specific capacitances.<sup>116</sup> Furthermore, we prepared An-CPOP1 and An-CPOP2 through simple Friedel–Crafts alkylations of An-4Ph with 2,4,6-trichloro-1,3,5-triazine and formaldehyde dimethyl acetal as crosslinker reagents.<sup>117</sup> An-CPOP1 possessed a tubular nanotube structure, based on SEM imaging, while An-CPOP2 displayed a capacitance of  $98.10\text{ F g}^{-1}$  at  $0.5\text{ A g}^{-1}$ . Mohamed *et al.* prepared DPT-HPP through a Friedel–Crafts reaction of (4-(5,6-diphenyl-1H-benzimidazol-2-yl)triphenylamine

in the presence of  $\text{FeCl}_3$ ; it exhibited a specific capacitance of  $110\text{ F g}^{-1}$  and excellent cycling stability over 2000 cycles.<sup>118</sup> We reported the TPPDATPPyr and TPPDA-TPTPE COFs prepared through Schiff-base condensations of TPPDA( $\text{NH}_2$ )<sub>4</sub> with TPPyr(CHO)<sub>4</sub> and TPTPE(CHO)<sub>4</sub>, respectively.<sup>119</sup> The TPPDATPPyr and TPPDA-TPTPE COFs were highly thermally resistant, with decomposition temperatures ( $T_{d10}$ ) of up to  $543$  and  $551^\circ\text{C}$ , respectively; in addition, they had high surface areas (up to  $1020$  and  $1067\text{ m}^2\text{ g}^{-1}$ , respectively). Both the TPPDATPPyr and TPPDA-TPTPE COFs underwent reversible redox processes at a low sweep rate ( $5\text{ mV s}^{-1}$ ) over the potential range from  $+0.18$  to  $-0.92\text{ V}$ , because of their redox-active triphenylamino groups. At a current density of  $2\text{ A g}^{-1}$ , the specific capacitance of the TPPDA-TPTPE COF ( $237.1\text{ F g}^{-1}$ ) was higher than that of the TPPDATPPyr COF ( $188.7\text{ F g}^{-1}$ ), due to the higher surface area of the former, as well as the easy access for electrolytes to its electrode surface, thanks to the presence of the heteroatoms. Furthermore, the TPPDATPPyr and TPPDA-TPTPE COFs displayed excellent cycling capacities, with retentions of up to  $86.2$  and  $85.6\%$ , respectively, after 5000 cycles. We have examined the effect of the COF surface area on capacitance through the formation of a sponge-like shell TPT-DAHQ COF through the template-free condensation of TPT-3CHO and DAHQ-2HCl.<sup>120</sup> The TPT-DAHQ COF possessed an



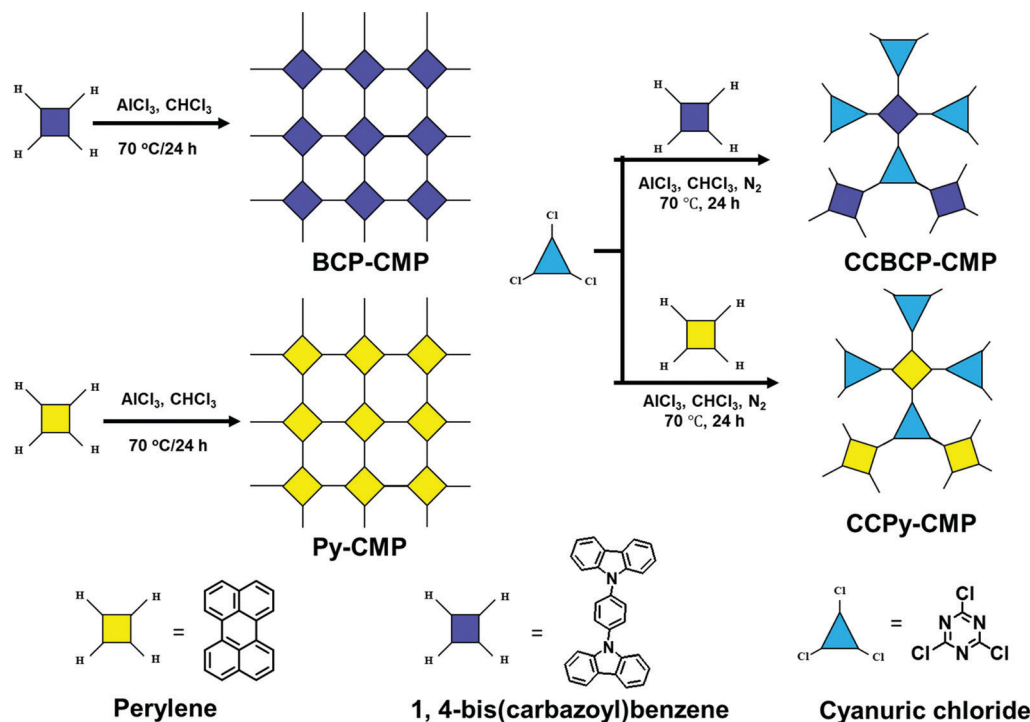


Fig. 13 Synthesis routes for BCP-CMP, Py-CMP, CCBCP-CMP and CCPy-CMP. Reproduced from ref. 108 with permission from Elsevier.

extraordinary surface area (up to  $1855 \text{ m}^2 \text{ g}^{-1}$ ) in addition to high thermal resistance (up to  $452 \text{ }^\circ\text{C}$ ). The high surface area of the TPT-DAHQ COF was the main factor behind its excellent capacitance (up to  $256 \text{ F g}^{-1}$  at current density of  $0.5 \text{ A g}^{-1}$ ); it displayed high durability, with up to 98.8% of its original capacitance retained without any obvious degradation after 1850 cycles at  $10 \text{ A g}^{-1}$ . We also elucidated the effect of the active redox sites in COFs structures through one-pot syntheses of three bifluorenylidene-based COFs BFTB-PyTA, BFTB-BFTB, and BFTB-BCTA through reactions of BFTB-4CHO with PyTA- $4\text{NH}_2$ , BFTB- $4\text{NH}_2$ , and BCTA- $4\text{NH}_2$ , respectively.<sup>113</sup> In addition to the BFTB-PyTA, BFTB-BFTB, and BFTB-BCTA COFs displaying record-high thermal resistances of up to 433, 416, and  $449 \text{ }^\circ\text{C}$ , respectively, they also exhibited high BET surface areas (up to  $1133$ ,  $1040$ , and  $834 \text{ m}^2 \text{ g}^{-1}$ , respectively), determined through  $\text{N}_2$  isothermal analyses at  $77 \text{ K}$ . The specific capacitances of the BFTB-PyTA and BFTB-BFTB COFs were  $68.0$  and  $84.5 \text{ F g}^{-1}$ , respectively, at a scan rate of  $5 \text{ mV s}^{-1}$ ; the specific capacitance of the BFTB-BCTA COF at the same scan rate was higher ( $89.9 \text{ F g}^{-1}$ ), although it had the lowest surface area, revealing that the redox-active sites were the carbazole subunits. Furthermore, the smooth surface morphology of the BFTB-BFTB COF played an important role in its specific capacitance being higher than that of the BFTB-PyTA COF, which had a hollow-microtubule structure. The capacitive retentions of the BFTB-PyTA, BFTB-BFTB, and BFTB-BCTA COFs were 97.27, 85.23, and 91.21%, respectively. Using our previously mentioned TFP-COFs, we investigated the effects of redox-active amino, pyridine, and carbazole groups on the reversible redox processes occurring at a low sweep rate of  $5 \text{ mV s}^{-1}$ . The specific capacitance of the TFP-TPA COF

(up to  $291.1 \text{ F g}^{-1}$ ) was higher than those of the TFP-TPP and TFP-Car COFs, due to its higher nitrogen-atom percentage; therefore, it had a greater number of available redox active sites, even though it had a lower surface area. The TFP-TPA COF, TFP-TPP and TFP-Car COFs exhibited high durability after 5000 cycles at  $10 \text{ A g}^{-1}$ , with retention of their original values of up to 91, 88.2, and 90.4%, respectively.<sup>105</sup> Triphenylamine has been a highly studied redox-active unit because of its ability to store energy. Our group investigated the previously mentioned COFs 1–6 to test their validity as supercapacitors. Indeed, the TPA-COFs 1–4 exhibited supercapacitance, whereas the TPT-COFs 5 and 6 did not provide any redox curves during cyclic voltammetry, consistent with their absence of triphenylamine moieties. Notably, the unsaturated  $\text{N}=\text{C}$  units do not display any reactivity in acidic media, and increasing the number of triphenylamine groups enhanced the specific capacitance; as a result, the capacitance of TPA-TPA-COF-1, which featured six triphenylamine groups, was higher than those of the other COFs 2–4. Morphologies and chemical structures can also play a role in affecting the specific capacitances of supercapacitors. We confirmed these phenomena in a recent study of the previously mentioned Car-TPA, Car-TPP, and Car-TPT COFs, which possessed carbazole, pyridine, and triphenylamine units, respectively, making them ideal candidates for storing energy; at  $0.2 \text{ A g}^{-1}$ , they displayed specific capacitances of 13.6, 14.5, and  $17.4 \text{ F g}^{-1}$ , respectively.<sup>103</sup> The Car-TPA and Car-TPP COFs had high surface areas and two redox groups, but provided lower capacitances; in contrast, the Car-TPT COF had a low surface area and only one redox group, but its microtubular structure and molecular design led to enhanced capacitance



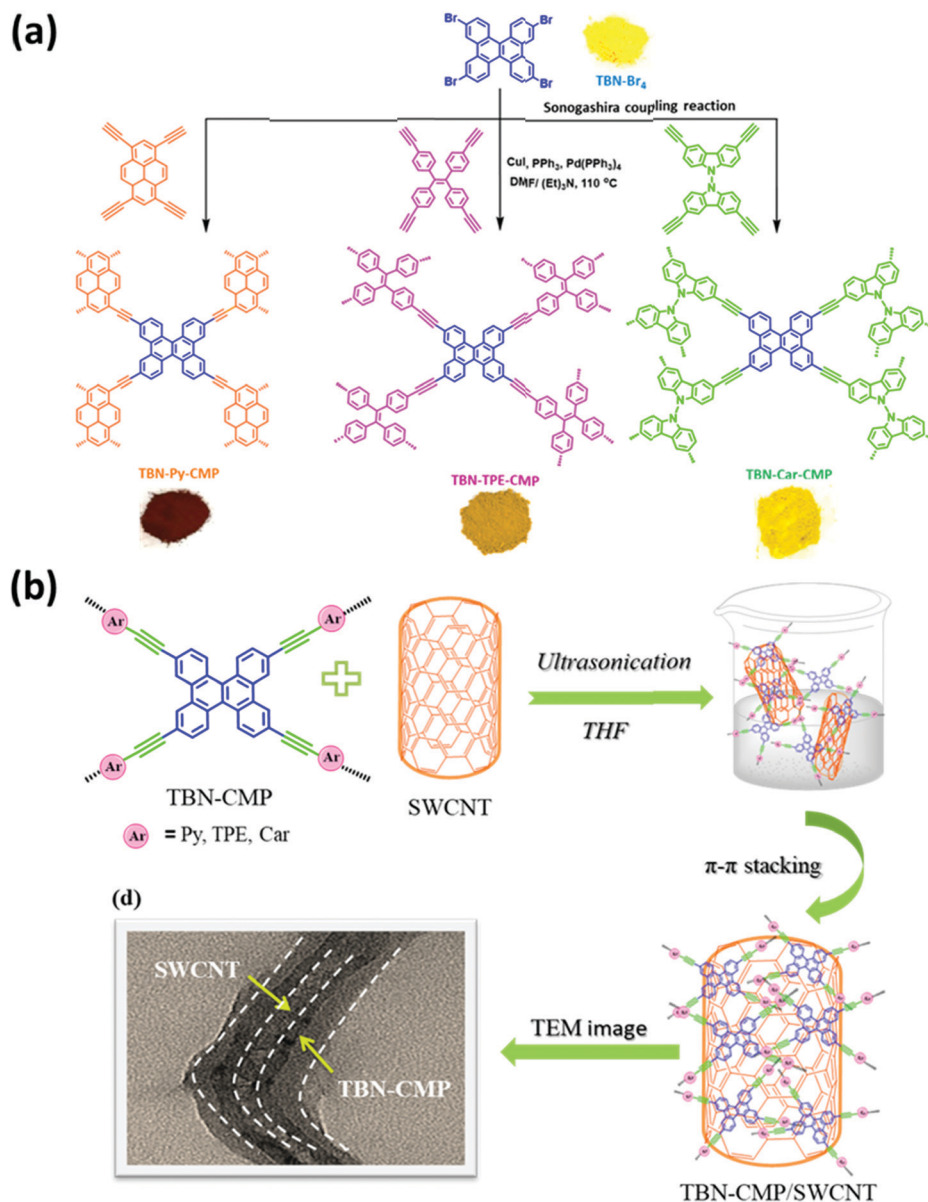


Fig. 14 (a) Synthesis of TBN-Py-CMP, TBN-TPE-CMP, and TBN-Car-CMP and (b) formation of TBN-CMP/SWCNTs. Reproduced from ref. 121 with permission from American Chemical Society.

and retention during the charging/discharging process. Recently, Maha *et al.* used Sonogashira-Hagihara reactions to prepare a series of CMPs based on tetrabenzonaphthalene (TBN) moieties (TBN-TPE-CMP, TBN-Py-CMP, and TBN-Car-CMP) [Fig. 14(a)].<sup>121</sup> Subsequently, we improved the conductivity of these materials by mixing them with single-walled carbon nanotubes (SWCNTs) [Fig. 14(b)]. Interestingly, the capacitance of the TBN-Py-CMP/SWCNT nanocomposite ( $430 \text{ F g}^{-1}$  at  $0.5 \text{ A g}^{-1}$ ) was higher than those of the other samples, presumably because of strong  $\pi$ - $\pi$  interactions between the pyrene units in the TBN-Py-CMP framework and the SWCNTs.<sup>122–125</sup> Eddaoudi *et al.* prepared Hex-Aza-COF-2 and Hex-Aza-COF-3 through solvothermal condensations of benzoquinone with redox-functionalized aromatic tetramines

and phenazine, respectively [Fig. 15(a)].<sup>126</sup> They used powder X-ray diffraction (PXRD), solid state NMR spectroscopy, BET analysis, SEM, and TEM imaging to investigate the chemical structures, crystallinities, porosities, and morphologies of these materials [Fig. 15(b)–(i)]. The PXRD data and SEM images revealed that both materials had moderate crystallinities and aggregated spherical morphologies. Furthermore, based on electrochemical measurements, the specific capacitances of Hex-Aza-COF-2 ( $585 \text{ F g}^{-1}$ ) and Hex-Aza-COF-3 ( $663 \text{ F g}^{-1}$ ) were higher than those reported previously for porous polymeric and COF materials. Yang *et al.* prepared a new porous organic HCP through the reaction of pyrene with  $\text{CHCl}_3$  as the crosslinker and  $\text{AlCl}_3$  as the catalyst, with the subsequent hydrolysis affording HcPPy that possessed a high surface area ( $723 \text{ m}^2 \text{ g}^{-1}$ ) and





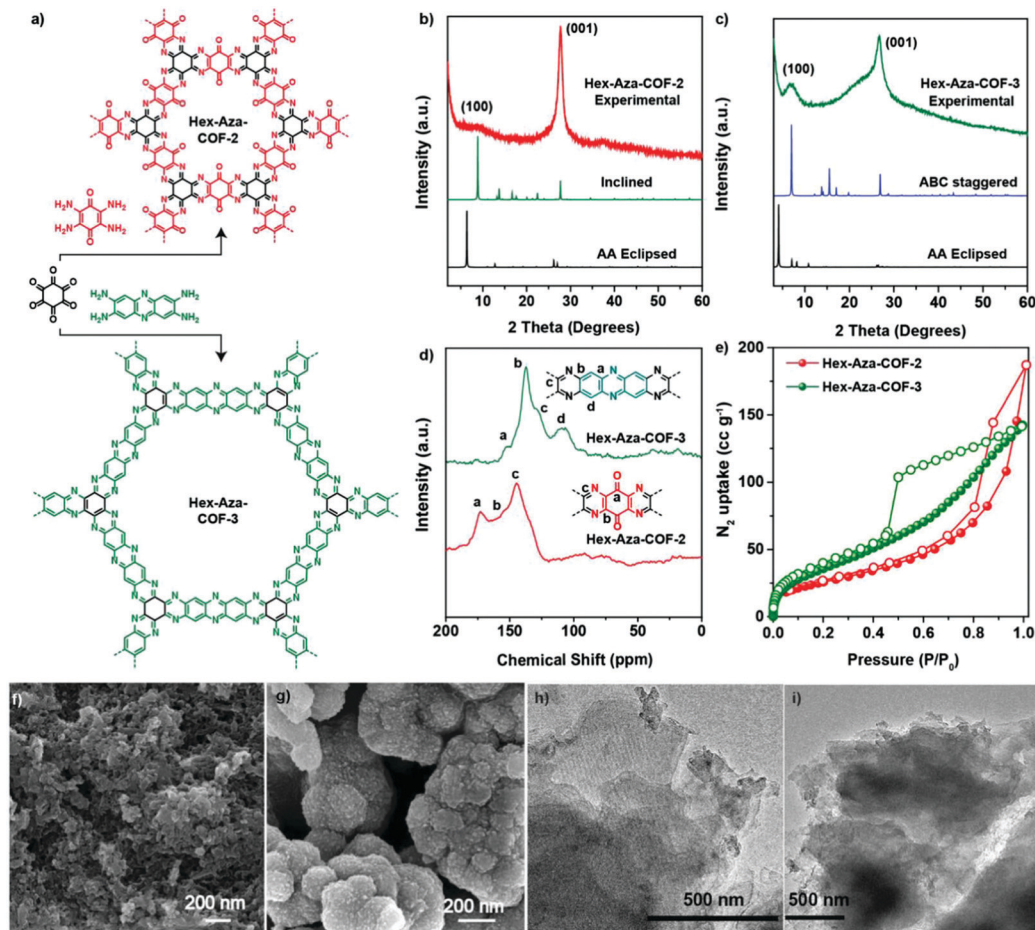


Fig. 15 (a) Synthesis of Hex-Aza-2 and Hex-Aza-COF-3, (b) and (c) PXRD pattern for Hex-Aza-COF-2 and Hex-Aza-COF-3. (d) Solid-state  $^{13}\text{C}$  NMR for Hex-Aza-COF-2 and Hex-Aza-COF-3. (e) BET isotherms for Hex-Aza-COF-2 and Hex-Aza-COF-3. (f and g) SEM images for Hex-Aza-COF-2 and Hex-Aza-COF-3. (h and i) TEM images for Hex-Aza-COF-2 and Hex-Aza-COF-3. Reproduced from ref. 126 with permission from Wiley-VCH.

micropores (1 nm) and mesopores (2–3 and 3.5–4.5 nm).<sup>127</sup> This material functioned as an anode in Li batteries and provided excellent current densities (up to  $683 \text{ MA h g}^{-1}$  at  $1000 \text{ mA g}^{-1}$ ). Wong *et al.* prepared materials named SP and HP through Sonogashira couplings of tri(4-ethynylphenylamine) with 9-ferrocenylidene-2,7-diiodo-9H-fluorene in the presence and absence of ZIF-67, respectively.<sup>128</sup> They then prepared Fe-embedded magnetic carbon materials (SP and HP-MCMs) through the carbonization of SP and HP at  $500^\circ\text{C}$  for 1 h. The obtained spherical SP-MCP had a microporous architecture, good redox performance, and good cycling stability when applied in lithium-ion batteries (LIBs) as an anode; its performance was superior to that of the HP-MCP. Zhao *et al.* prepared the 2D-COF-ETTA-ETTCA and COF-ETTA-ETTCA-S materials by loading 88.4 wt% of sulfur and applied these materials in lithium-sulfur batteries.<sup>129</sup> The devices displayed high capacity (up to  $1617 \text{ mA h g}^{-1}$  at 0.1C), low capacitance decay after 528 cycles, and high coulombic performance (*ca.* 98%).

### 3.4. Hydrogen evolution

Chi *et al.* synthesized a new electrochemical material ( $\text{PMO}_{10}\text{V}_2@\text{CTF}$ ) through the fabrication of  $\text{PMO}_{10}\text{V}_2$  with a

cationic CTF as a support, itself prepared through trimerization of 1,3-bis(4-cyanophenyl)imidazolium chloride.  $\text{PMO}_{10}\text{V}_2@\text{CTF}$  functioned as the catalyst for the production of benzaldehyde and  $\text{H}_2$  through the oxidation of benzyl alcohol.<sup>130</sup> Recently, der Voort *et al.* prepared metal-free electrocatalysts based on porous BINOL-CTF materials featuring various nitrogen-containing groups (pyridine-N-oxide, pyrrolic-N, quaternary-N, and pyridinic-N/triazine-N units) through cyclization reactions of 2,2'-dihydroxy[1,1'-binaphthalene]-6,6'-dicyanitrile as the C and N atom sources in molten  $\text{ZnCl}_2$  at 400 and  $500^\circ\text{C}$ , respectively.<sup>131</sup> BINOL-10-500 displayed outstanding performance in the hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR), relative to the other CTF samples, as a result of its large pores, high specific surface area, and high quaternary-N content. Recently, COFs have garnered an exciting position in the field of  $\text{H}_2$  production because of their ability to facilitate charge transfer and light harvesting. Accordingly, our group applied two of the previously mentioned COFs (PyTA-BC, and PyTA-BC-Ph), based on their excellent photophysical properties, as photocatalysts for  $\text{H}_2$  evolution from water in the presence of a sacrificial electron donor. The PyTA-BC and PyTA-BC-Ph COFs provided photocatalytic activities of up to



1183 and 417  $\mu\text{mol g}^{-1} \text{h}^{-1}$ , respectively, in the presence of ascorbic acid as the electron donor.<sup>132</sup> Jiang *et al.* prepared, through the *in situ* growth of TFPT-DETH on the octahedral  $\text{NH}_2\text{-UiO-66}$  surface, an  $\text{NH}_2\text{-UiO-66@TFPT-DETH}$  core-shell hetero-framework possessing an octahedral morphology, a smooth surface, a high surface area, light absorption properties, and both meso- and microporous structures; it mediated a high degree of  $\text{H}_2$  production from water (up to 7178  $\text{mmol g}^{-1} \text{h}^{-1}$ ) (Fig. 16).<sup>133</sup> Interestingly, Guo *et al.* prepared multivariate  $\text{Tp}(\text{BTxTP}_{1-x})\text{-COFs}$  for photocatalytic  $\text{H}_2$  evolution from water through condensation of the monomer 1,3,5-triformylphloroglucinol (Tp) with tertiary phenyl (TP) and benzothiadiazole-derived (BT) units [Fig. 17(a)].<sup>134</sup> FTIR and solid state NMR spectroscopy confirmed the chemical structures of the resulting COFs, which possessed highly crystalline structures and high surface areas ( $>700 \text{ m}^2 \text{ g}^{-1}$ ) [Fig. 17(b)-(e)]. The  $\text{H}_2$

evolution rate increased to 9839  $\mu\text{mol g}^{-1} \text{h}^{-1}$  when the COF material contained 5 mol% of BT.

### 3.5. Chemical sensing

Laskar *et al.* prepared two branched conjugated mesoporous polymers (CMO1 and CMO2) displaying aggregation-induced emission and high quantum yields.<sup>135</sup> CMO1 was more sensitive than CMO2 towards trinitrotoluene (TNT) and picric acid, due to the higher pore density and size in CMO1. The Zhong group prepared a highly fluorescent F-CTF-3 porous framework through the condensation of phenamidine hydrochloride with 4,4'-(benzo[*c*][1,2,5]thiadiazole-4,7-diyl)dibenzaldehyde.<sup>136</sup> This fluorescent material functioned as a chemical sensor for phenylamine (PA) and phenylenediamine (PDA), with detection at concentrations of 11.7 and 1.47 nM, respectively. The excellent luminescence features of COFs can arise in addition to

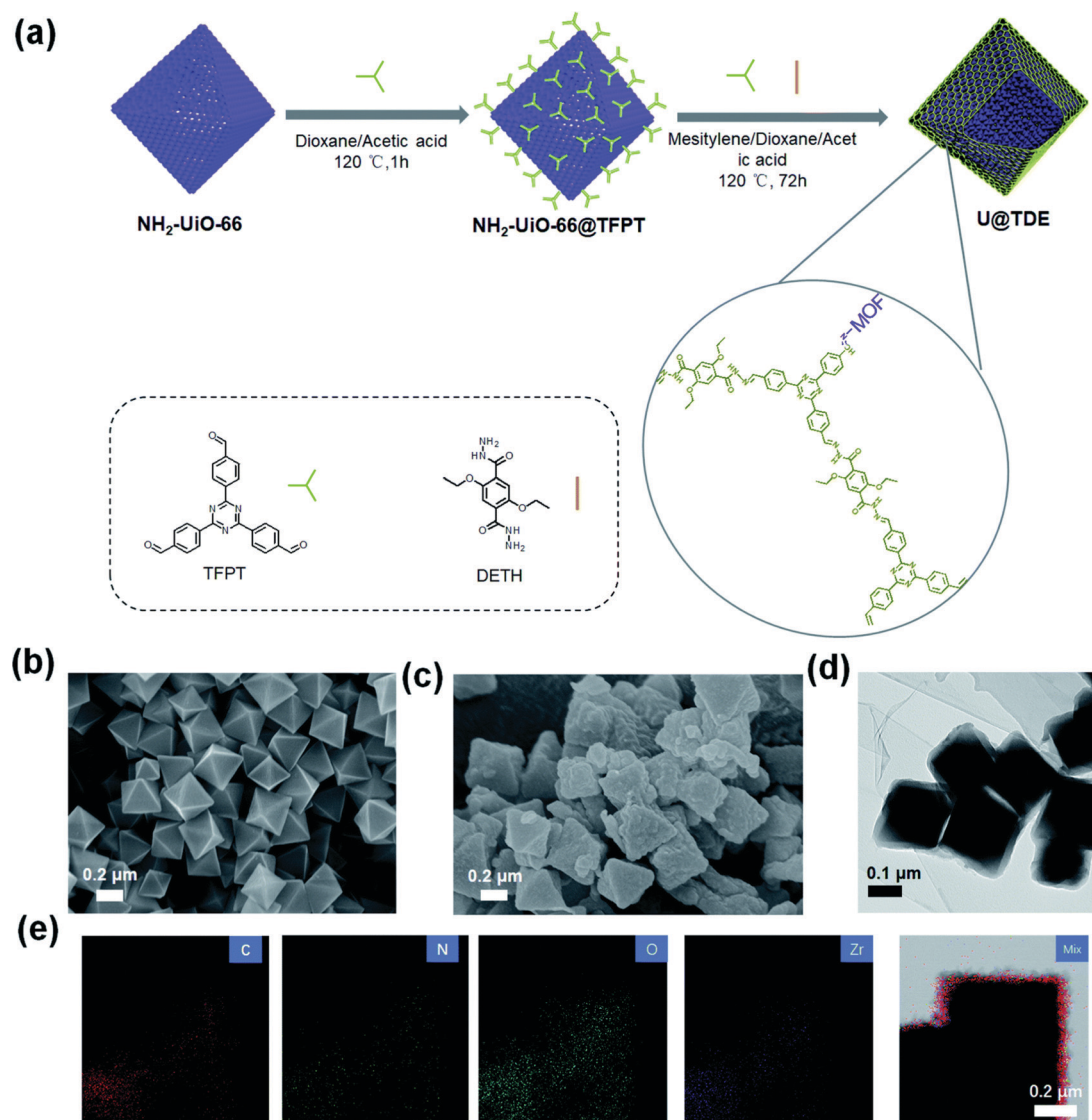


Fig. 16 (a) Schematic for the preparation of  $\text{U@TDE}_n$  core-shell hetero frameworks. (b) SEM image of  $\text{NH}_2\text{-UiO-66}$ ; (c) SEM, (d) TEM image and (e) EDX mapping of  $\text{U@TDE}_4$ . Reproduced from ref. 133 with permission from the Royal Society of Chemistry.



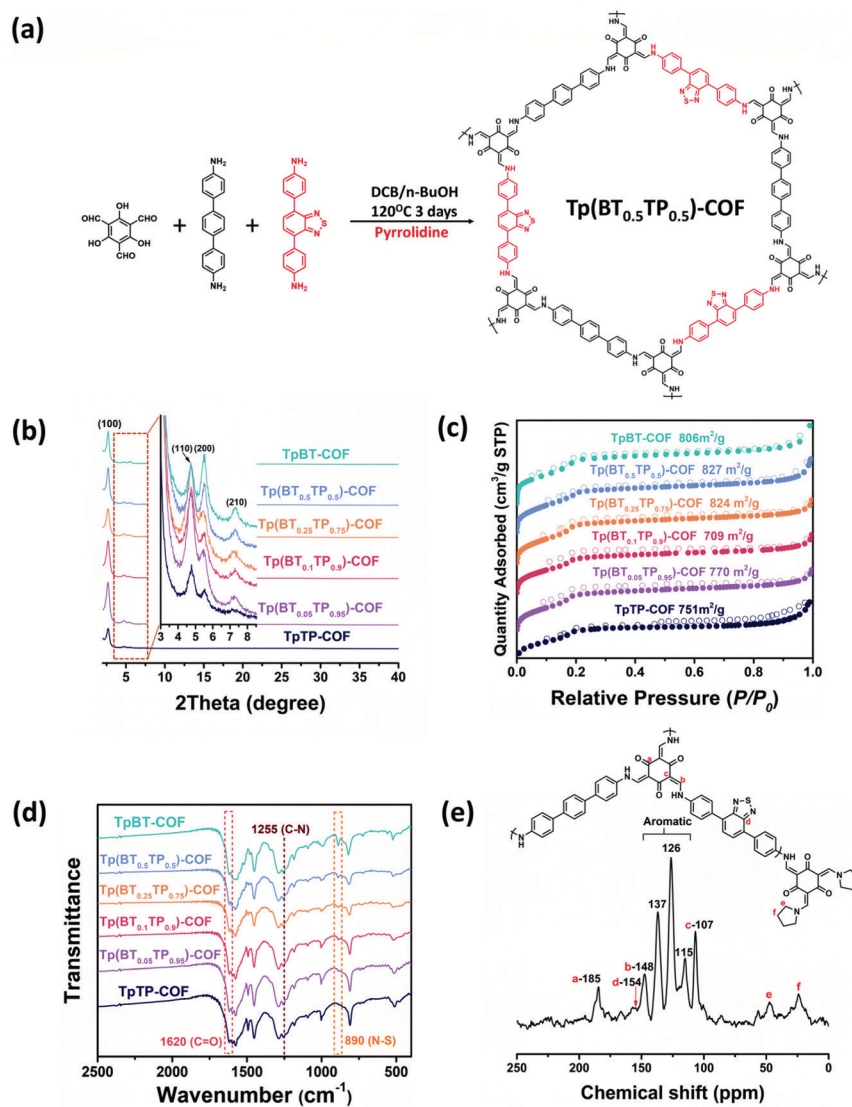


Fig. 17 Synthesis of  $\text{Tp}(\text{B}_x\text{TP}_{1-x})\text{-COFs}$ . (b)–(d) PXRD,  $\text{N}_2$  adsorption–desorption and FT-IR profiles of  $\text{Tp}(\text{B}_x\text{TP}_{1-x})\text{-COFs}$ . (e) Solid-state  $^{13}\text{C}$  CP/MAS NMR spectrum of  $\text{Tp}(\text{BT}_{0.05}\text{TP}_{0.95})\text{-COF}$ . Reproduced from ref. 134 with permission from the Royal Society of Chemistry.

their low densities, high chemical stabilities, and high thermal stabilities, making them promising candidates for use as fluorescent sensors. Often,  $\pi$ -conjugation of the building blocks (e.g., triazine, carbazole, pyrene, and triphenylene) or the inherently rigid structure of the COFs leads to this fluorescence behavior. We reported the first applicable COF for the detection of amino acids. We used solvothermal conditions to prepare a  $\text{Cu}@\text{TFPB-DHTH}$  COF (Fig. 18) through polycondensation of TFPB-3CHO and DHTH and subsequent modification with  $\text{Cu}^{2+}$  ions.<sup>137</sup> The BET surface area of the TFPB-DHTH COF was  $360 \text{ m}^2 \text{ g}^{-1}$ ; it displayed high thermal stability up to  $322 \text{ }^\circ\text{C}$ . The TFPB-DHTH COF exhibited highly fluorescent yellow emission in addition to high chemical stability; the addition of  $\text{Cu}^{2+}$  ions quenched this fluorescence, due to aggregation. Anions had only marginal effects on this quenching. The fluorescence intensity increased upon the addition of cysteine and *L*-histidine. The limits of detection (LODs) for cysteine and *L*-histidine in the

presence of the  $\text{Cu}@\text{TFPB-DHTH}$  COF were 340 and 520 nM, respectively, with high selectivity. Fluorescent COFs have also been used for the spectroscopic determination of very low concentrations (nanomolar) of HCl. We have fabricated the three luminescent COFs BCTB-PD, BCTA-TP, and BCTB-BCTA through Schiff base condensations of BCTB-4CHO with PD, BCTA-4NH<sub>2</sub> with TP, and BCTB-4CHO with BCTA-4NH<sub>2</sub>, respectively.<sup>138</sup> The thermal stabilities of the BCTB-PD and BCTB-BCTA COFs were higher than that of the BCTA-TP COF, revealing the positive effect of BCTB-4CHO as the aldehydic building block. The BET surface areas of the BCTB-PD, BCTB-BCTA, and BCTA-TP COFs were 2212, 1098, and  $645 \text{ m}^2 \text{ g}^{-1}$ , respectively. Noncovalent interactions (hydrogen bonding, dipole effects) between these COFs and polar solvents led to red-shifting upon increasing the solvent polarity, in addition to enhancing the stability of the excited states of the COFs and, hence, their corresponding intramolecular charge transfer (ICT). The BCTB-4CHO-based COFs (BCTB-PD and BCTB-BCTA)





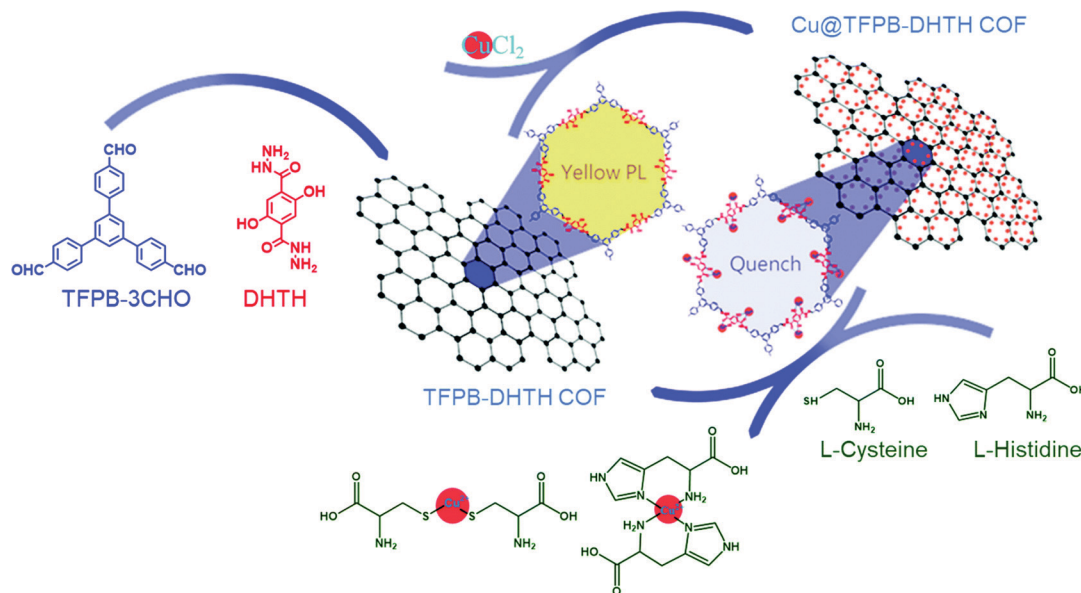


Fig. 18 Schematic representation of Cu@TFPB-DHTH COF as a chemical sensor for Cys and L-His. Reproduced from ref. 137 with permission from the Royal Society of Chemistry.

displayed fluorescence emissions because their BCTB-4CH=N units functioned as electron donating groups that facilitated ICT between the carbazole BCTB-4CH=N units and the acceptors; in contrast, the weakly electron donating BCTA-4N=CH groups resulted in weak fluorescence for the BCTA-TP COF. The BCTB-BCTA COF displayed high fluorescence sensitivity for the detection of HCl, due to the increasing planarity of its constituent units upon protonation of the imino nitrogen atoms in the BCTB-BCTA COF architecture, resulting in red-shifting of the signal. The fluorescence lifetime of the BCTB-BCTA COF increased from 4.13 to 4.89 ns upon exposure to 1 mmol L<sup>-1</sup> HCl, in addition to displaying an LOD of 10 nmol L<sup>-1</sup>. Increasing the planarity of the units in the COFs and converting them into quinoid structures were exploited by our group for HCl sensing using 2D PyTA-BC and PyTA-BC-Ph COFs, prepared through Schiff base condensations of PyTA-4NH<sub>2</sub> with BC-4CHO and BC-Ph-4CHO, respectively, and separately under solvothermal conditions.<sup>125</sup> The PyTA-BC and PyTA-BC-Ph COFs had thermal stabilities of up to 403 and 421 °C, respectively, and high surface areas (520 and 1445 m<sup>2</sup> g<sup>-1</sup>, respectively); we attribute the superior thermal stability and surface area of the PyTA-BC-Ph COFs to their longer building blocks. Both the PyTA-BC and PyTA-BC-Ph COFs exhibited solvatochromism phenomena and red-shifting of their signals occurred, due to strong hydrogen bonding between the amino groups on the COF surfaces and the C=O groups of the polar solvents, which facilitated ICT. Interactions of the PyTA-BC and PyTA-BC-Ph COFs with HCl also induced red-shifting from their original yellow color; the signals reverted back after exposure to NH<sub>3</sub> vapor. This process, which could be repeated without considerable performance loss, resulted from the increase in planarity upon protonation and the formation of quinoid structures. The PyTA-BC and PyTA-BC-Ph COFs had very low LODs for HCl of 24 and 20 nmol L<sup>-1</sup>, respectively.<sup>132</sup> Guo *et al.* obtained a

new 1D-COF with a specific surface area of 426 m<sup>2</sup> g<sup>-1</sup> and thermal stability up to 360 °C through the reaction of TFPpy and DABP; they used this COF as a chemical H<sup>+</sup> sensor in acidic solutions.<sup>139</sup> Zhu *et al.* prepared a dual-luminescent COF (DL-COF) through Schiff base formation between ETTA and 9,10-anthracenedicarboxaldehyde and used it for the chemical sensing of explosive nitro compounds with high selectivity and sensitivity.<sup>140</sup> Mohamed *et al.* used Heck reactions to prepare the four ultrastable microporous polymers An-HPP, TPT-HPP, Car-HPP, and TPE-HPP from octavinylsilsesquioxane (OVS) and brominated anthracene triphenyltriazine, bicarbazole, and tetraphenylethene, respectively; we revealed that these materials displayed good thermal stabilities because of the presence of the inorganic POSS units and the high crosslinking densities.<sup>141–144</sup> Furthermore, these four fluorescent materials could be used for the detection of Fe<sup>3+</sup> ions.

### 3.6. Other applications

Ning *et al.* prepared two CMPs containing organic dyes in their backbones through Sonogashira couplings of TDFB and TCT with TEB (Fig. 19).<sup>145</sup> The TDFB-TEB CMP possessed a narrower band gap and a more planar  $\pi$ -conjugated structure and displayed higher photocatalytic performance towards the aerobic oxidants sulfur and amines with excellent recycling, compared with the behavior of TCT-TEF. Ma *et al.* reported CMP-S1, a CMP containing aromatic naphthalene moieties and a conjugated structure, that exhibited higher performance for aromatic capture than that for alkanes, based on organic vapor adsorption analysis.<sup>146</sup> Xia *et al.* synthesized pTTT-BTD, pTTT-Ben, and pTTT-DMOB CMPs from 2,4,6-(tri-2-thienyl)-1,3,5-triazine as the knot block and the linkers BTD, Ben, and BMOB, respectively, each with different morphologies and electronic and optical properties. Interestingly, pTTT-Ben exhibited high





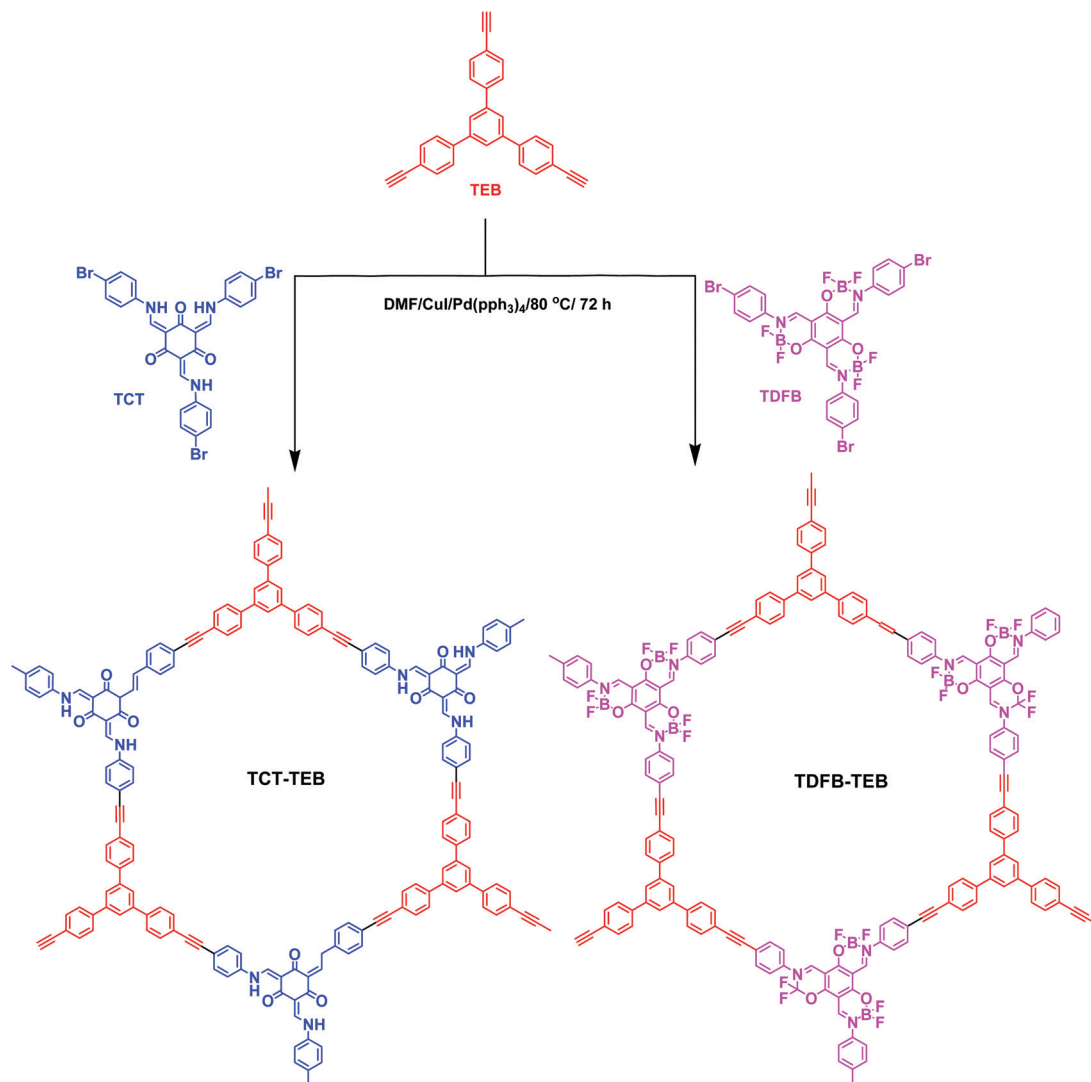


Fig. 19 Preparation of TDFB-TEB and TCT-TEB. Reproduced from ref. 145 with permission the Royal Society of Chemistry.

photocatalytic performance, providing high production rates of succinic acid ( $4.66 \text{ mmol g}^{-1} \text{ h}^{-1}$ ) and 2,5-diformylfuran ( $0.53 \text{ mmol g}^{-1} \text{ h}^{-1}$ ) from biomass materials.<sup>147</sup> Zhang *et al.* incorporated phosphoric acid into porous solids through Sonogashira coupling of 1,3,5-tris(4-ethynylphenyl)benzene with various aliphatic perfluoro monomers (Fig. 20).<sup>148</sup> The obtained electrolytes of the CMP polymers had a low activation energy (0.4 eV) and high proton conductivity ( $4.39 \times 10^{-3} \text{ S cm}^{-1}$ ), due to their hydrophobic pores and hydrogen bonding between phosphoric acid and the perfluoroalkyl chains of the CMPs. Zhao *et al.* obtained the thiazolo[5,4-*d*]thiazole-linked CMPs TZTZ-TA and TZTZ-TP through condensations of 1,3,5-tri(4-formylphenyl)benzene with 2,4,6-tri(4-formylphenyl)-1,3,5-triamine (as the  $C_3$  symmetrical anode block) and with dithiooxamide (as the  $C_2$  monomer), respectively.<sup>149</sup> The obtained CMPs had amorphous characteristics, different colors, good thermal stabilities, and BET surface areas in the range from 314.8 to  $439.5 \text{ m}^2 \text{ g}^{-1}$ . Furthermore, the TZTZ-TA CMP containing the triazine units mediated

the production of NADH (82.0 wt% within 5 min) to an outstanding degree when compared with that of TZTZ-TP (6.9 wt% during 10 min). Lang *et al.* prepared a different series of CMPs, based on fluorene and carbazole units as electron donating groups, and observed that MFC-CMP displayed a high BET specific surface area, more sites for oxidation, and good performance in the production of imines and oxygen through amine oxidation under visible light photocatalysis.<sup>150</sup> Hua and co-workers used Sonogashira coupling to prepare a series of fluorescent CMPH, CMPNH<sub>2</sub>, and CMPN materials containing amino groups. CMPN, which featured *N,N*-diethylpropylamine units as side chains in the framework, exhibited good I<sub>2</sub> capacity and excellent stability towards  $\beta$ - and  $\gamma$ -ray irradiation, which was the result of the formation of charge-transfer complexes between I<sub>2</sub> and the amino, phenyl, and triazine groups.<sup>151</sup> Maji *et al.* constructed a CMP containing dithienyl units as photochromic groups through Schiff-base condensation of dithienylethene aldehyde and benzene-1,3,5-tricarboxyhydrazide [Fig. 21(a)].<sup>152</sup> They investigated its porosity, chemical structure, morphology, and



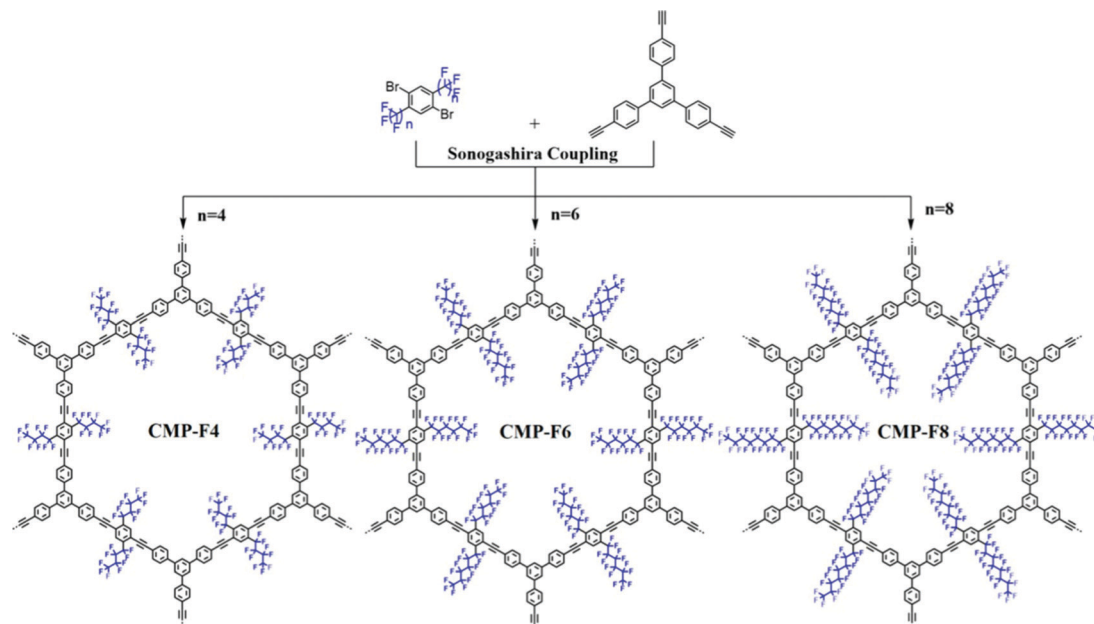


Fig. 20 Synthesis of perfluoroalkyl-functionalized CMPs. Reproduced from ref. 148 with permission from American Chemical Society.

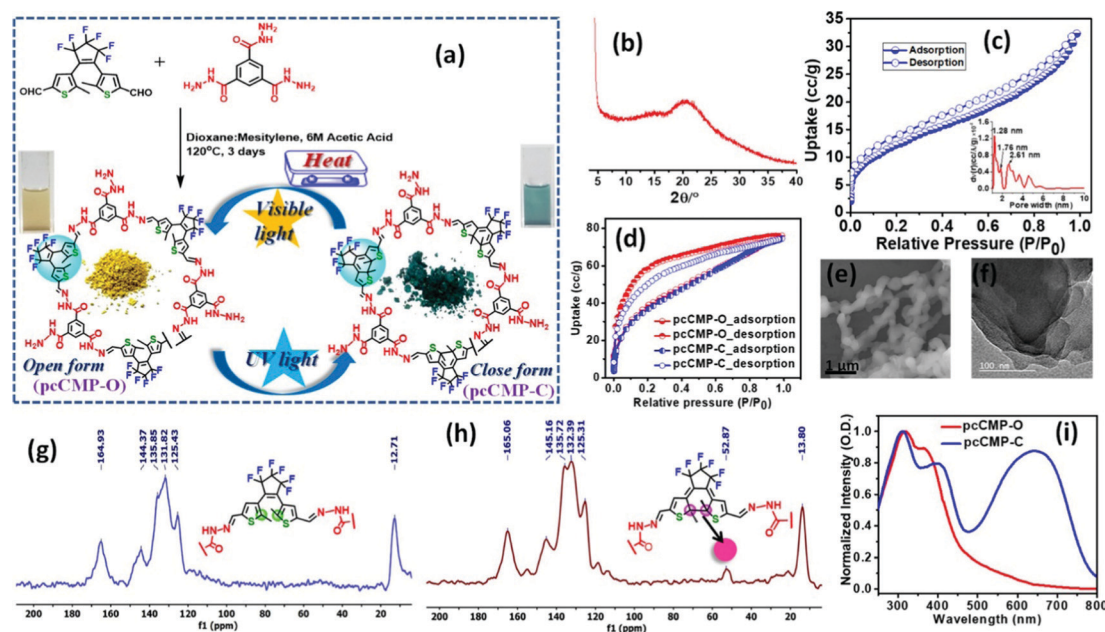


Fig. 21 (a) Preparation of the pcCMP (b) PXRD for pcCMP-O; (c) N<sub>2</sub> adsorption (77 K) for pcCMP-O; (d) CO<sub>2</sub> adsorption for pcCMP-O and pcCMP-C; (e) FESEM and (f) TEM images for pcCMP-O; (g) and (h) solid-state <sup>13</sup>C NMR for pcCMP-O and pcCMP-C, respectively; and (i) UV-vis absorption spectra in the solid state for pcCMP-O and pcCMP-C. Reproduced from ref. 152 with permission from American Chemical Society.

optical and crystallinity properties [Fig. 21(e)–(t)]. The pcCMP-O structure had a yellow color that, after UV irradiation, changed to give the deep-green pcCMP-C; in addition, pcCMP-O functioned as an NH function logic gate. Li and co-workers prepared a metal-free heterogeneous catalyst (2,5-DCP-CTF) through the cyclotrimerization of 2,5-dicyanopyridine in the presence of molten ZnCl<sub>2</sub>.<sup>153</sup> 2,5-DCP-CTF possessed a high nitrogen atom content and a hierarchical porous structure; they used it for the

preparation of cyclic carbonates with high selectivity and for the conversion of CO<sub>2</sub>. Hu *et al.* used silicon-promoted cationic polymerization to synthesize a series of HCPs with outstanding chemical stability, surface area, tunable porosity, and extended conjugation, which were capable of capturing dibenzothiophene (1335 mg g<sup>-1</sup>).<sup>154</sup> Hou *et al.* prepared TFPPy-Td-COFs with a high surface area (1094 m<sup>2</sup> g<sup>-1</sup>) and uniform pore size (2.87 nm) through the condensation of TFPPy with thiazazole-2HN<sub>2</sub>.<sup>155</sup>



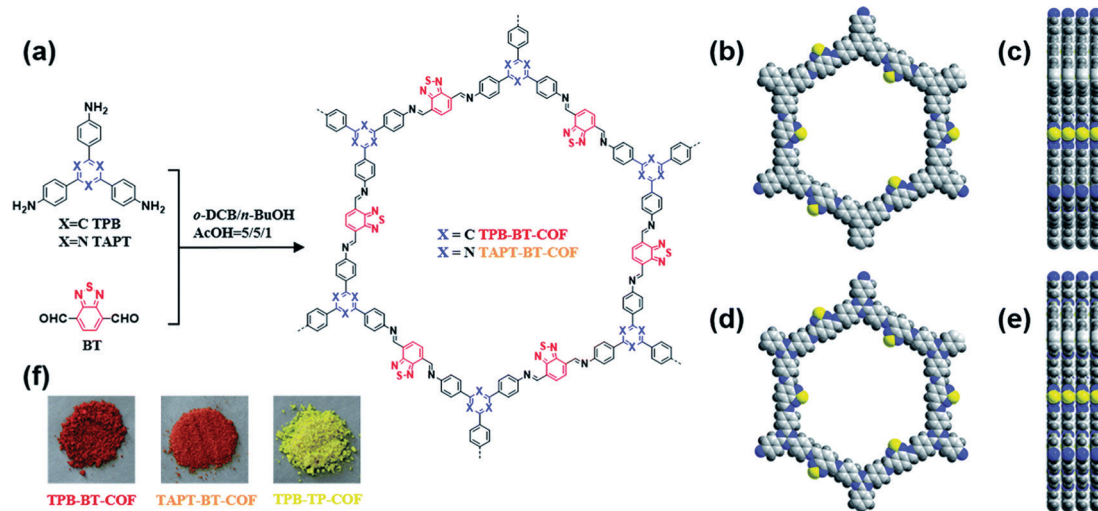


Fig. 22 (a) Synthesis of BT-COFs; (b) top and (c) side view of TPB-BT-COF; (d) top and (e) side view of TAPT-BT-COF; (f) photographs of TPB-BT-COF, TAPT-BT-COF and TPB-TP-COF. Reproduced from ref. 156 with permission from the Royal Society of Chemistry.

Interestingly, they prepared polymethylacrylates with a narrow polydispersity index when using TFPPy-Td-COFs as a heterogeneous photocatalyst for atom transfer radical polymerization (ATRP) photo-induced polymerization under irradiation with white light in the presence of Cu(I). In 2019, Chen *et al.* prepared two kinds of donor-acceptor 2D-COFs (TPB-BT-COF, and TAPT-BT-COF), featuring benzothiadiazole (BT) units as electron acceptors, through condensation reactions (Fig. 22).<sup>156</sup> These materials possessed outstanding porosities, were chemically stable under strongly acidic and basic conditions, and had high crystallinities. The rate of photoreduction of an aqueous solution of hexavalent chromium [Cr(VI)] in the presence of the TPB-BT-COF was faster than that in the presence of the TAPT-BT-COF, due to the former having a narrower band gap and an abundant negative conduction band, allowing facile migration and separation of hole

pairs/photogenerated electrons. In 2020, Jiang *et al.* synthesized the sp<sup>2</sup>-N enriched TM-TPT-COF through the reaction of TM with TPT in the presence of a basic catalyst.<sup>157</sup> They then prepared Pt@COF through the reaction of the TM-TPT-COF with K<sub>2</sub>PtCl<sub>4</sub>; the presence of Pt NPs in the COF layers was confirmed using high-resolution TEM (HR-TEM), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy, and WT-extended XAFS (EXAFS). The ORR mediated by the fabricated Pt@COF electrocatalyst in an acidic electrolyte was superior to that of a commercial Pt/C catalyst. In 2020, Huang *et al.* constructed a 2D-COF based on porphyrin units (TAPP-TFPP-COF) from the reaction of TAPP with TFPP; it exhibited excellent crystallinity, stability, tetragonal micropores, a high BET surface area of 962 m<sup>2</sup> g<sup>-1</sup> and a pore size of 1.8 nm (Fig. 23).<sup>158</sup> The conductivity of the TAPP-TFPP-COF after doping with I<sub>2</sub> increased from 1.12 × 10<sup>-10</sup>

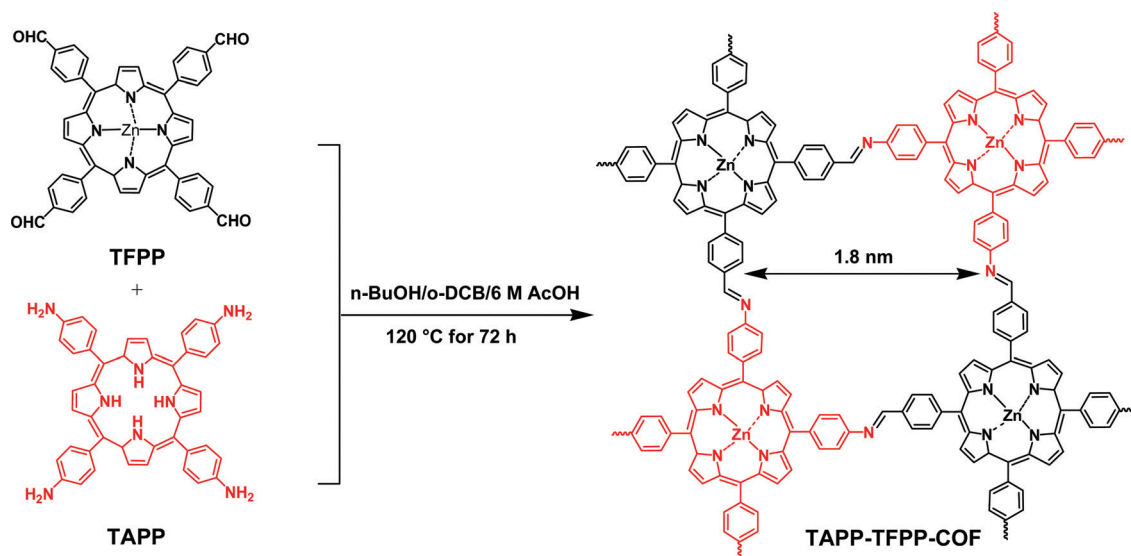


Fig. 23 Synthesis of microporous TAPP-TFPP-COF. Reproduced from ref. 158 with permission from American Chemical Society.



to  $1.46 \times 10^{-7} \text{ S cm}^{-1}$ ; furthermore, TAPP-TFPP-COF films displayed high sensitivity and selectivity at 700 nm, based on spectroscopic detection. Our group contributed to the development of perovskite solar cells through the preparation of the 2D-COFs Car-ETTA and TFPPy-ETTA through [4+4] solvothermal condensations of ET TA with Car-4CHO and TFPPy, respectively. The Car-ETTA and TFPPy-ETTA COFs possessed high thermal stabilities (up to 467 and 580 °C, respectively) and high surface areas (829 and 1156  $\text{m}^2 \text{g}^{-1}$ , respectively). Perovskite solar cells modified with the Car-ETTA and TFPPy-ETTA COFs displayed high power conversion efficiencies (PCEs), up to 19.79 and 19.72%, respectively, resulting from minimized charge recombination at the perovskite-PTAA-COF interfaces, due to low energy levels of the highest occupied molecular orbitals of the COFs.<sup>159</sup>

## 4. Conclusion and Outlook

POPs, including CTFs, COFs, HCPs, and CMPs, are attractive porous materials, and are comparable with metal-organic framework inorganic zeolites, because they possess excellent chemical and thermal stabilities, low densities, and tunable porosities, while being easy to prepare with flexible designs and structural diversity. These porous materials have been applied as useful platforms in many fields, including energy storage and conversion, gas separation, chemical sensing, luminescence, electronic devices, drug delivery, and  $\text{H}_2$  evolution from water. In this review, we discuss many examples of recent progress in the preparation of these materials, as well as the excellent performance of some POPs applied for  $\text{CO}_2$  uptake, energy storage,  $\text{H}_2$  evolution, photocatalysis, and photovoltaics. In the past few years, many research groups have prepared such materials with excellent properties; nevertheless, the use of novel synthetic methods for the preparation of new CMPs, CTFs, and COF remains worthwhile. For example, even COF materials with Frank-Kasper phases or Archimedean tiling patterns could have specific applications, and are interesting to consider. Finally, further exploration of the properties and applications of new POP materials will continue to open doors in both academia and industry.

## Author contributions

The manuscript was written through contributions from all authors.

## Abbreviation

An	Anthracene
BTD	Benzothiadiazole
Ben	Benzene
BD	Benzidine
BT	Benzothiadiazole
Cz-4CHO	Bi-carbazole-4CHO
Car-4CN	[9,9'-Bicarbazole]-3,3',6,6'-tetracarbonitrile

An-4Ph	9,10-Bis(diphenylmethylene)-9,10-dihydroanthracene
BFTB-4CHO	4,4',4'',4'''-[[9,9'-Bifluorenylidene]-3,3',6,6'-tetrayl] tetrabenzaldehyde
BFTB-4NH <sub>2</sub>	4,4',4'',4'''-[[9,9'-Bifluorenylidene]-3,3',6,6'-tetrayl]tetraaniline
BCTA-4NH <sub>2</sub>	4,4',4'',4'''-[[9,9'-Bicarbazole]-3,3',6,6'-tetrayl]tetraaniline
BCTB-4CHO	4,4',4'',4'''-[[9,9'-Bicarbazole]-3,3',6,6'-tetrayl]tetrabenzaldehyde
BC-Ph-4CHO	4,4',4'',4'''-[[9,9'-Bicarbazole]-3,3'',6,6''-tetrayl]tetrabenzaldehyde
TCNPy	1,3,6,8-Cyanopyrene
$\text{CO}_2$	Carbon dioxide
OVS	Cubic octavinylsilsesquioxane
CTFs	Covalent triazine frameworks
COFs	Covalent organic frameworks
CMPs	Conjugated microporous polymers
DHBD	3,3'-Dihydroxybenzidine
DAHQ-2HCl	2,5-Diaminohydroquinone dihydrochloride
DHTH	2,5-Dihydroxyterephthalohydrazide
BMOB	Dimethoxybenzene
DABP	4,4'-Diaminobenzophenone
$\gamma$ -CD	$\gamma$ -Cyclodextrin
ETTA	4,4',4'',4'''-(Ethane-1,1,2,2-tetrayl)tetranilino
$\text{H}_2$	Hydrogen
$\text{H}_2\text{O}_2$	Hydrogen peroxide
HCPs	Hypercrosslinked polymers
htb	Hexagonal tungsten bronze
hxl	Hexagonal layer
kgm	Kagome
IUPAC	International Union of Pure and Applied Chemistry
ICT	Intramolecular charge transfer
Li-S	Lithium-sulfur batteries
LiOH	Lithium hydroxide
MOFs	Metal-organic frameworks
NTCDA	1,4,5,8-Naphthalenetetracarboxylic dianhydride
PS	Polystyrene
Py	Pyrene
POPs	Porous organic polymers
PAFs	Porous aromatic frameworks
PIMs	Polymers of intrinsic microporosity
PMDA	Pyromellitic dianhydride
PA	Phenylamine
PDA	Phenylenediamine
PD	<i>p</i> -Phenylenediamine
PyTA-4NH <sub>2</sub>	4,4',4'',4'''-(Pyrene-1,3,6,8-tetrayl)tetraaniline
PyTA-4NH <sub>2</sub>	4,4',4'',4'''-Pyrene-1,3,6,8-tetrayl]tetraaniline
SEM	Scanning electron microscope
TEM	Transmission electron microscope
TGA	Thermogravimetry analyses
TfOH	Trifluoromethanesulfonic acid
Car-3NH <sub>2</sub>	Triamine 9-(4-aminophenyl)-carbazole-3,6-diamine





TPA-3CHO	Tris(4-formylphenyl)amine
TPP-3CHO	2,4,6-Tris(4-formylphenyl)pyridine
TPT-3CHO	2,4,6-Tris(4-formylphenyl)triazine
TPA-3NH <sub>2</sub>	Tris(4-aminophenyl)amine
TPT-3NH <sub>2</sub>	2,4,6-Tris(4-aminophenyl)triazine
TFP-3OHCHO	1,3,5-Triformylphloroglucinol
TAPA	Tris(4-aminophenyl)amine
TAPB	1,3,5-Tris(4-aminophenyl)benzene
TPPDA(NH <sub>2</sub> ) <sub>4</sub>	Tetraphenyl- <i>p</i> -phenylenediamine
TPPy(CHO) <sub>4</sub>	1,3,6,8-Tetrakis(4-formylphenyl)pyrene
TPTPE(CHO) <sub>4</sub>	1,1,2,2-Tetrakis[4-formyl-(1,1'-biphenyl)]ethane)
TBN	Tetrabenzonaphthalene
TP	1,3,5-Triformylphloroglucinol
TPE	Tetraphenylethene
Pyr-4Ph	Tetraphenylpyrazine
TNT	Trinitrotoluene
TFPB-3CHO	1,3,5-Tris(4-formylphenyl)benzene
BC-4CHO	3,3',6,6''-Tetraformyl-9,9''-bicarbazole
TFPPy	1,3,6,8-Tetrakis( <i>p</i> -formylphenyl)pyrene
TP	Terephthalaldehyde
TPT	Triphenyltriazine
Ben-T	1,3,5-Tris(4-ethynylphenyl)benzene
TM	2,4,6-Trimethyl-1,3,5-triazine
Car-4CHO	3,3',6,6''-Tetraformyl-9,9''-bicarbazole
B(OMe) <sub>3</sub>	Trimethyl borate
sql	Square lattice
SBU	Secondary building units
SWCNTs	Single walled carbon nanotubes
TAPP	Zinc 5,10,15,20-tetra(4-aminophenyl)porphyrin
TFPP	Zinc 5,10,15,20-tetra(4-formylphenyl)porphyrin

## Conflicts of interest

The authors declare that they have no conflicts of interest.

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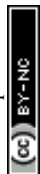
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