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Triptycene-like naphthopleiadene as a readily accessible scaffold for supramolecular and materials chemistry†

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Triptycene derivatives are used extensively in supramolecular and materials chemistry, however, most are prepared using a multi-step synthesis involving the generation of a benzyne intermediate, which hinders production on a large scale. Inspired by the ease of the synthesis of resorcinarenes, we report the rapid and efficient preparation of triptycene-like 1,6,2',7'-tetrahydroxynaphthopleiadene directly from 2,7-dihydroxynaphthalene and phthalaldehyde. Structural characterisation confirms the novel bridged bicyclic framework, within which the planes of the single benzene ring and two naphthalene units are fixed at an angle of $\sim 120^\circ$ relative to each other. Other combinations of aromatic 1,2-dialdehydes and 2,7-disubstituted naphthalenes also provided similar triptycene-like products. The low cost of the precursors and undemanding reaction conditions allow for rapid multigram synthesis of 1,6,2',7'-tetrahydroxynaphthopleiadene, which is shown to be a useful precursor for making the parent naphthopleiadene hydrocarbon. The great potential for the use of the naphthopleiadene scaffold in supramolecular and polymer chemistry is demonstrated by the preparation of a rigid novel cavitand, a microporous network polymer, and a solution-processable polymer of intrinsic microporosity.

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Introduction

Triptycene is a bridged bicyclic hydrocarbon composed of three benzene rings fused to two sp^3 hybridised carbon bridgeheads (Fig. 1).^{1–3} The symmetry and rigidity of triptycene results in its derivatives being used extensively as scaffolds in supramolecular^{4–10} and materials chemistry.^{11–20} For example, triptycenes are key components in molecular machines (such as gears,^{21–24} brakes,²⁵ rotors²⁶), crystal engineering,^{27,28} macrocycles,^{7,29,30} cages,^{31–33} optoelectronic materials,^{34–40} self-assembling monolayers at interfaces,^{41–45} and ligands for metal catalysts.^{46–50} The shape of triptycene, with the three benzene rings fused at an angle of 120° relative to each other, is particularly attractive for providing the vertices within ordered porous materials such as 2D honeycomb-like polymers,^{51,52} molecular crystals,^{53,54} nanotubes,⁵⁵ covalent organic frameworks,^{56–58} and metal organic frameworks.^{26,59} However, our long-term interest in triptycene derivatives has been in their use as monomers for making amorphous Polymers of Intrinsic Microporosity (PIMs),^{60–63} an interest which is shared with

several other research groups.^{64–71} PIMs exploit the rigidity⁷² of triptycene and the internal molecular free volume (IMFV)⁷³ that originates from its concavities (Fig. 1). Triptycene-derived PIMs have great potential for making high performance gas separation membranes.^{74,75} Indeed, data from these polymers define the current upper bounds for the trade-off between permeability and selectivity for the separation of several important gas pairs,^{76,77} including those of interest for post combustion carbon capture and natural gas purification.⁷⁸

For the diverse applications listed above, the triptycene component generally requires a multi-step synthesis and laborious chromatographic purification of intermediates and product.^{79,80} Despite some newly developed methods,^{81–85} triptycene and its derivatives are still predominantly prepared by the Diels–Alder reaction between an anthracene derivative and a reactive benzyne intermediate.^{86,87} It should be noted that even unsubstituted triptycene is an expensive starting material, presumably due to the inherent difficulties and hazards in scaling-up reactions involving benzyne.^{88,89} Frustrated by the time-consuming preparation of triptycene monomers for making PIMs, we are developing methods for their rapid synthesis that can be readily performed on a large-scale. Here we report the simple one-step synthesis of a triptycene-like compound, which has a novel bridged bicyclic framework composed of a single benzene and two naphthalene units fused to two carbon bridging atoms, for which we propose the name naphthopleiadene (NP, Fig. 1). The readily prepared derivative

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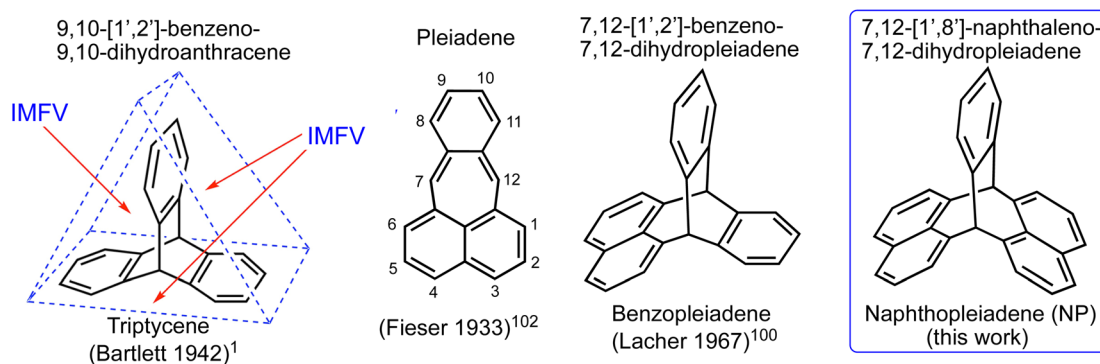


Fig. 1 The structure and nomenclature of triptycene, pleiadene and the two triptycene-like molecular frameworks obtained from the formal fusing of either benzene or naphthalene, *via* two of its *peri*-carbons, to the 7,12 sites of pleiadene. The intramolecular free volume (IMFV)⁷³ is indicated for triptycene and this will be enhanced for naphthopleiadene due to the greater width of the naphthalene units.

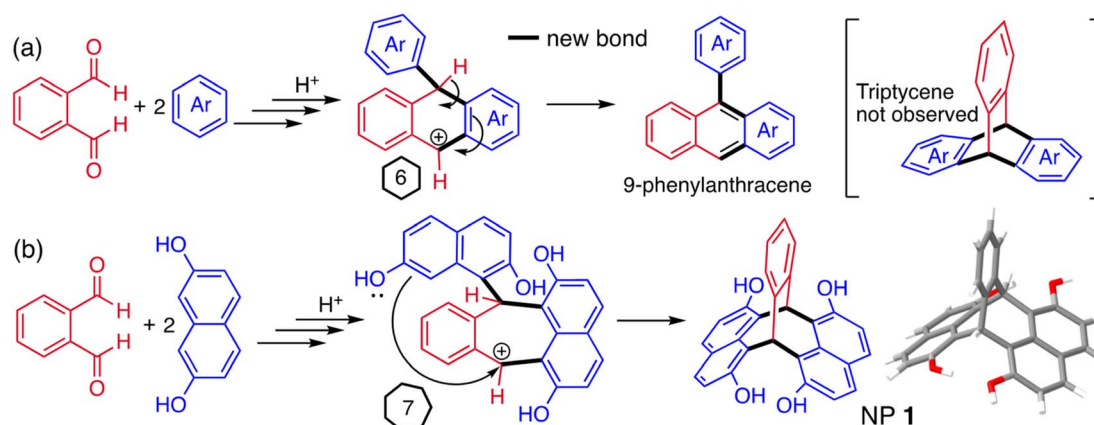


Fig. 2 Proposed partial mechanisms for (a) formation of 9-phenylanthracenes from the reaction between phthalaldehyde and benzene derivatives (Ar) *via* a carbocation containing in a six-membered ring,⁹⁰ and (b) the reaction between phthalaldehyde and 2,7-dihydroxynaphthalene to give naphthopleiadene 1 (NP 1), *via* a carbocation contained within a seven-membered ring which cannot aromatise *via* loss of proton.

NP 1 (Fig. 2), which contains in-built hydroxyl functionality, is useful for further synthetic elaboration as demonstrated by the synthesis of a very rigid cavitant, a microporous network polymer, a solution-processable PIM, and the unsubstituted NP hydrocarbon (Fig. 4).

Results and discussion

Acid-mediated reactions between aldehydes and electron-rich aromatic compounds were considered for the synthesis of triptycene derivatives, similar to those used for the efficient assembly of resorcinarenes (ESI Fig. 1†).^{91–93} Naïvely, it was anticipated that these could be formed from the double addition of an appropriate aromatic compound to phthalaldehyde, however, literature reports of such reactions with benzene derivatives present no evidence of any triptycene product.^{90,94–97} Instead, it is proposed that 9-phenyl anthracenes are produced *via* a carbocation contained within a six-membered ring, from which the loss of a proton enables the efficient formation of the extended aromatic system (Fig. 2a). On consideration of this mechanism, it was reasoned that a triptycene-like product may

be formed if the reaction pathway to 9-phenylanthracene could be blocked by avoiding the six-membered ring intermediate. For example, the double addition of 2,7-dihydroxynaphthalene to phthalaldehyde was anticipated to form a carbocation intermediate contained within a seven-membered ring, which would not be compatible with aromatization (Fig. 2b).

Using reaction conditions optimised for the synthesis of resorcinarenes (ESI Fig. 1†),^{98,99} heating an acidified ethanol solution of a 2 : 1 mole ratio of 2,7-dihydroxynaphthalene and phthalaldehyde rapidly produced a colourless solid. Intriguingly, ¹H and ¹³C NMR analysis showed that a highly symmetric product was obtained in high purity. A single crystal X-ray diffraction study confirmed the formation of a novel bridged bicyclic framework with two sp³ hybridised bridging carbons, to which are fused a single benzene ring and two naphthalene units, the latter at their *peri*-(1,8)-positions. Like triptycene, the planes of the three fused aromatic units are fixed at an angle of ~120° relative to each other (Fig. 2b). The related triptycene-like framework, consisting of two benzene rings and a single naphthalene unit, was reported in 1967.^{100,101} This bridged bicyclic compound was considered a derivative of the



unsaturated hydrocarbon pleiadene,^{102,103} for which the seven-membered ring evoked the Pleiades of Greek mythology, therefore, it was named 7,12-(1',2'-benzo)-7,12-dihydropleiadene (Fig. 1).^{100,101} Using the same IUPAC endorsed nomenclature,¹⁰⁴ we suggest the systematic name of 7,12-(1',8'-naphthaleno)-7,12-dihydropleiadene for the novel molecular framework, and the trivial name naphthopleiadene (NP) for the parent hydrocarbon (Fig. 1), the synthesis of which is described below (Fig. 4).

Optimisation of the reaction conditions for the synthesis of 1,6,2',7'-tetrahydroxynaphthopleiadene (NP 1) indicated that only a few drops of concentrated aqueous HCl (37%) are required and that simple alcohols perform best as solvent (ESI Table 1†). NP 1 was produced directly in good yield (~70%, first crop) and required no further purification except for the removal of alcohol in a drying oven. Additional product (~20%, second crop) can be obtained by removal of the solvent from the filtrate followed by recrystallisation. Remarkably, the maximum yield is produced within only a few minutes after heating to reflux. Alternatively, a similar yield and purity of product was obtained at ambient temperature, but the reaction took longer to complete (~24 h). The low cost of the precursors and undemanding reaction conditions allows for large-scale synthesis

with, for example, 70 g of NP 1 being obtained easily (ESI Table 1 and Fig. 2†). Water as reaction solvent gave a good crude yield but the resulting solid contained a purple impurity, which required recrystallisation from ethanol to remove, therefore, negating any potential benefits from its use.

Replacement of phthalaldehyde in the reaction with 2,3-naphthalenedialdehyde or 1,2-thiophenedialdehyde also provided triptycene-like products 2 and 3, respectively (Fig. 3). Similarly, 2-hydroxy-7-methoxynaphthalene reacts with phthalaldehyde to give a mixture of the isomeric products 1,7'-dihydroxy-6,2'-dimethoxy-naphthopleiadene (**4a**) and 1,2'-dihydroxy-6,7'-dimethoxy-naphthopleiadene (**4b**), which could be separated by using the relatively poor solubility of the former in acetone. The same reaction conditions using 2,7-dimethoxynaphthalene and phthalaldehyde failed to provide 1,6,2',7'-tetramethoxynaphthopleiadene (**5**). However, by adapting an efficient preparation of methoxy-substituted triphenylmethanes,¹⁰⁵ using $\text{BF}_3 \cdot \text{OEt}_2$ in dichloromethane, NP 5 was obtained in moderate yield with its structure also confirmed by single crystal XRD analysis.

The structure of NP 1, with a short distance between adjacent hydroxyl groups (O to O distance = 2.74 Å), suggested a similar reactivity to that of the resorcinarenes, for which Cram

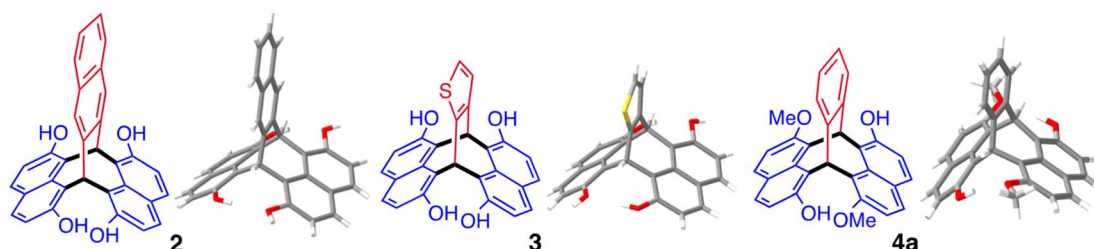


Fig. 3 The structures derived from single crystal; XRD of triptycene-like compounds 2, 3 and 4a.

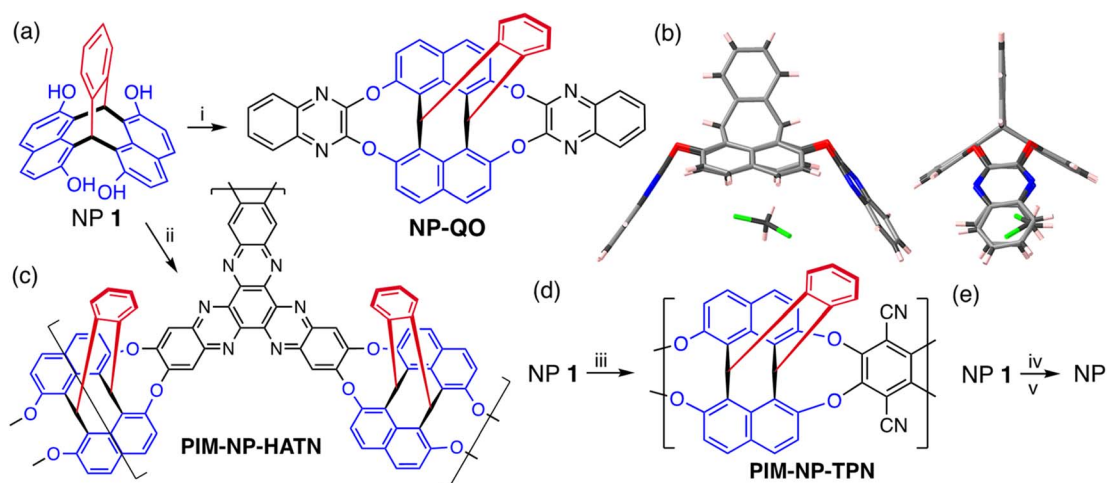


Fig. 4 (a) The synthesis of cavitant NP-QO from NP 1: (i) 2,3-dichloroquinoxaline, K_2CO_3 , DMF, 80 °C, 48 h, yield 100%. (b) Two views of the XRD structure of cavitant NP-QO showing the included CH_2Cl_2 molecule. (c) The synthesis of an ultramicroporous network polymer PIM-NP-HATN: (ii) 2,3,8,9,14,15-hexafluoro-5,6,11,12,17,18-hexaazatrinaphthylene, K_2CO_3 , DMF, 120 °C, 48 h, yield 86%. (d) The synthesis of soluble PIM-NP-TPN: (iii) 2,3,5,6-tetrafluoroterephthalonitrile, K_2CO_3 , DMF, 30–120 °C, 160 h, yield 84%. (e) (iv) Trifluoromethanesulfonic anhydride, pyridine, 25 °C, 16 h. (v) $\text{Pd}(\text{OAc})_2$, 1,3-bis(diphenylphosphino)propane, Et_3SiH , DMF, 60 °C, 1 h.



demonstrated deep cavitand formation using the efficient reaction with 2,3-dichloroquinoxaline (ESI Fig. 1†).¹⁰⁶ Similarly, the reaction between NP 1 and 2,3-dichloroquinoxaline proceeds in very high yield *via* the formation of two nine-membered tribenzo-1,4-dioxonine rings (Fig. 4a). A single crystal XRD analysis of the product **NP-QO** shows a symmetrical cavitand-like structure that contains a single molecule of dichloromethane held within the cavity (Fig. 4b). Unlike Cram's deep cavitands, which exists in rapidly exchanging *vase* and *kite* conformers,^{92,107} the structure of **NP-QO** appears fully fixed by the NP framework. Indeed, simple molecular mechanical modelling suggest that the conformer produce by the inversion of a single tribenzo-1,4-dioxonine ring is ~ 60 kJ mol⁻¹ higher in energy due to the steric effect of the NP bridgehead hydrogen (ESI Fig. 3†).

The highly efficient formation of the tribenzo-1,4-dioxonine unit, demonstrated by the synthesis of cavitand **NP-QO**, suggested that polymers may also be prepared by similar aromatic nucleophilic substitution reactions. Hence, the synthesis of both a network and a non-network polymer was attempted by the reactions between NP 1 and 2,3,8,9,14,15-hexafluoro-5,6,11,12,17,18-hexaazatrinaphthylene¹⁰⁸ or 2,3,5,6-tetrafluorophthalonitrile, respectively (Fig. 4c and d), with structural characterisation performed by solid-state NMR (ESI Fig. 4†). Thermal Gravimetric Analysis (TGA) of both polymers showed a mass loss of only $\sim 27\%$ at 850 °C, providing very high char yields that are consistent with the predominately aromatic structure of the polymers (ESI Fig. 5†). For the resulting network polymer **NP-HATN**, there was low N₂ adsorption at 77 K with the shape of the isotherm suggesting slow rate of uptake (ESI Fig. 6†). However, an impressive CO₂ uptake of 3.3 mmol g⁻¹ at 1 bar (273 K) suggests significant microporosity with the pore size distribution being predominantly ultramicroporous (<0.7 nm), which combined with high rigidity, severely reduces the rate of N₂ adsorption (ESI Fig. 7†). Gas adsorption of the powdered form of the non-network polymer **NP-TPN** confirmed intrinsic microporosity with significant N₂ uptake at 77 K allowing an apparent S_{BET} of 635 m² g⁻¹ and total pore volume of 0.40 ml g⁻¹ to be estimated. It may be that the non-network structure of **PIM-NP-TPN** allows some swelling during N₂ adsorption, which facilitates greater total uptake. **PIM-NP-TPN** proved soluble in polar aprotic solvents, and once the polymerisation was optimised, a high average molecular mass ($M_n = 140\,000$ g mol⁻¹) was obtained as measured by gel permeation chromatography. Despite this, only brittle self-standing films of **PIM-NP-TPN** could be cast from DMF solution, which proved too fragile for gas permeability measurements. It should be noted that the ability to fabricate robust self-standing films from many PIMs, despite their fused ring structures, has been attributed to the relative flexibility of the dibenzodioxane linking group.¹⁰⁹ However, a comparison of the flexibility of the dibenzodioxane linking group with that of tribenzo-1,4-dioxonine, using molecular mechanical modelling (ESI Fig. 8†), suggests that the latter is much more rigid, which is likely to be detrimental to the film forming properties of **PIM-NP-TPN**. Nevertheless, a solution-processable PIM, that contains cavitand-like structures, may be useful for making adsorbents

or sensors and, hence, microporous polymers derived from NP 1 is the focus of continuing work.¹¹⁰

As suggested by a reviewer, the viability of using NP 1 as a precursor for making the previously unreported parent NP hydrocarbon (Fig. 1) was established by using the proto-dehalogenation of its pseudohalide triflate ester (Fig. 4e).¹¹¹ Although optimisation of this reaction is required, the successful synthesis of NP was confirmed by ¹H and ¹³C NMR and high-resolution mass spectroscopy. It was found that the chemical shift of the ¹H NMR signal for the bridgehead hydrogens of the resulting NP ($\delta_H = 5.4$ ppm, ESI Fig. 15†) is similar to those of triptycene and benzopleiadene.¹⁰¹ In comparison, the bridgehead hydrogens of NPs 1–5 are strongly deshielded relative to those of unsubstituted NP with values in the range 6.8–7.3 ppm, similar to those reported for triptycene derivatives that also contain hydroxyl or methoxy groups adjacent to the bridgehead.^{50,112,113} The bridgehead hydrogens of **NP-QO** have an extraordinary chemical shift of 8.79 ppm, which may be attributed to the electron-withdrawing nature of the quinoxaline unit combined with the effect of its ring current.

Conclusions

With the increasing complexity of modern synthetic chemistry, it is gratifying to obtain a novel compound, which possesses both an interesting structure and useful reactivity, from a very simple reaction between two readily available precursors. The ease in which NP 1 is prepared suggests that it will have further applications beyond cavitand and microporous polymer synthesis. For example, NP 1 could replace various hydroxylated triptycene precursors, each of which require a complex multi-step synthesis,¹¹⁴ in the preparation of pincer catalysts⁵⁰ and materials for which the structure and properties are controlled by triptycene self-assembly. Potential target materials include liquid crystals,¹¹² highly ordered thin-films¹¹³ and polymers with unusual mechanical properties.^{12,14,115} As noted by Swager, triptycene self-assembly is driven by the requirement to eliminate intermolecular free volume (IMFV), thus favouring the interlocking of triptycene units.^{17,18} As the naphthalene units of NP generate larger IMFV than the benzene rings of triptycene (Fig. 1), the NP component may enhance self-assembly in these materials, in addition to being suitable for scale-up for commercial development. Finally, like their 2,7-dihydroxynaphthalene and 2,7-dimethoxynaphthalene precursors, solutions of NP 1 and NP 5 show visible blue fluorescence (ESI Fig. 16 and 17†), which may form the basis for applications in sensing.¹¹⁶

Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data has been deposited at the CCDC with the following accession numbers: NP 1 (2286805); NP 2 (2286808); NP 3 (2286809); NP 4a (2286807); NP 5 (2286804) and **NP-QO** (2286806) and can be obtained from <https://www.ccdc.cam.ac.uk/structures/>.



Author contributions

MKA led the synthetic effort. CY prepared **PIM-NP-TPN**, SP prepared NP 5. YL prepared NP 2 and its precursor. DT and SP prepared the NP parent hydrocarbon. DT obtained the UV/Visible and fluorescence spectra. GSN carried out single crystal XRD analysis, NBM conceived the project and wrote the first draft of the manuscript. All authors contributed to writing the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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References

- P. D. Bartlett, M. J. Ryan and S. G. Cohen, Triptycene (9,10-*o*-benzenoanthracene), *J. Am. Chem. Soc.*, 1942, **64**, 2649–2653.
- M. Woźny, A. Mames and T. Ratajczyk, Triptycene derivatives: from their synthesis to their unique properties, *Molecules*, 2022, **27**, 250.
- L. W. Zhao, Z. Li and T. Wirth, Triptycene derivatives: synthesis and applications, *Chem. Lett.*, 2010, **39**, 658–667.
- J. H. Chong and M. J. MacLachlan, Iptycenes in supramolecular and materials chemistry, *Chem. Soc. Rev.*, 2009, **38**, 3301–3315.
- Y. Han, Z. Meng, Y.-X. Ma and C.-F. Chen, Iptycene-derived crown ether hosts for molecular recognition and self-assembly, *Acc. Chem. Res.*, 2014, **47**, 2026–2040.
- J. Li, X.-N. Han, H.-Y. Zhou, Y. Han and C.-F. Chen, Helic[1] triptycene[3]arene: synthesis, complexation, and formation of [2]rotaxane shuttle, *J. Org. Chem.*, 2020, **85**, 11465–11474.
- Y. He, X. Yang, M. Qi and C. Chen, Triptycene-derived heterocalixarene: a new type of macrocycle-based stationary phases for gas chromatography, *Chin. Chem. Lett.*, 2021, **32**, 2043–2046.
- S. Hasegawa, A. Baksi, B. Chen and G. H. Clever, Guest encapsulation scope of a triptycene-based Pd₂L₄ coordination cage, *Organic Materials*, 2022, **4**, 222–227.
- M. Kato, T. Fukui, H. Sato, Y. Shoji and T. Fukushima, Capturing the trajectory of metal-ion-cluster formation: stepwise accumulation of Zn(II) ions in a robust coordination space formed by a rigid tridentate carboxylate ligand, *Inorg. Chem.*, 2022, **61**, 3649–3654.
- Z. Liu, W. Song, S. Yang, C. Yuan, Z. Liu, H.-L. Zhang and X. Shao, Marriage of heterobuckybowls with triptycene: molecular waterwheels for separating C₆₀ and C₇₀, *Chem.-Eur. J.*, 2022, **28**, e202200306.
- T. M. Swager, Iptycenes in the design of high performance polymers, *Acc. Chem. Res.*, 2008, **41**, 1181–1189.
- F. Ishiwari, G. Okabe, H. Ogiwara, T. Kajitani, M. Tokita, M. Takata and T. Fukushima, Terminal functionalization with a triptycene motif that dramatically changes the structural and physical properties of an amorphous polymer, *J. Am. Chem. Soc.*, 2018, **140**, 13497–13502.
- L. Xie, R. Yang, N. Li, P. Froimowicz and K. Zhang, Competitive study of novel triptycene-containing benzoxazine monomers and a thermoresponsive linear main chain-type benzoxazine copolymer: synthesis, polymerization, and thermal properties of their thermosets, *Macromolecules*, 2022, **55**, 6973–6981.
- J. Yu, A. Itagaki, Y. Chen, T. Fukui, F. Ishiwari, T. Kajitani and T. Fukushima, Effective design for long-range polymer ordering using triptycene-containing side chains, *Macromolecules*, 2023, **56**, 4556–4565.
- E. Hoffmeister, J. E. Kropp, T. L. McDowell, R. H. Michel and W. L. Rippie, Triptycene polymers, *J. Polym. Sci., Part A: Polym. Chem.*, 1969, **7**, 55–63.
- F. Akutsu, M. Inoki, M. Kondo, T. Inagawa, K. Kayaki and Y. Kasashima, Synthesis and properties of novel polyarylates and poly(ether ether ketone)s derived from 2,7-triptycenediol, *Polym. J.*, 1997, **29**, 1023–1028.
- N. T. Tsui, A. J. Paraskos, L. Torun, T. M. Swager and E. L. Thomas, Minimization of internal molecular free volume: a mechanism for the simultaneous enhancement of polymer stiffness, strength, and ductility, *Macromolecules*, 2006, **39**, 3350–3358.
- N. T. Tsui, L. Torun, B. D. Pate, A. J. Paraskos, T. M. Swager and E. L. Thomas, Molecular barbed wire: threading and interlocking for the mechanical reinforcement of polymers, *Adv. Funct. Mater.*, 2007, **17**, 1595–1602.
- Y. C. Liu, S. R. Turner and G. Wilkes, Melt-phase synthesis and properties of triptycene-containing copolyesters, *Macromolecules*, 2011, **44**, 4049–4056.
- S. Mondal and N. Das, Triptycene based organosoluble polyamides: synthesis, characterization and study of the effect of chain flexibility on morphology, *RSC Adv.*, 2014, **4**, 61383–61393.
- W. D. Hounshell, C. A. Johnson, A. Guenzi, F. Cozzi and K. Mislow, Stereochemical consequences of dynamic gearing in substituted bis(9-triptycyl) methanes and related molecules, *Proc. Natl. Acad. Sci. U. S. A.*, 1980, **77**, 6961–6964.
- X. Jiang, S. Yang, M. J. Jellen, K. N. Houk and M. Garcia-Garibay, Molecular spur gears with triptycene rotators and a norbornane-based Stator, *Org. Lett.*, 2020, **22**, 4049–4052.
- Y. Gisbert, S. Abid, C. Kammerer and G. Rapenne, Molecular gears: from solution to surfaces, *Chem.-Eur. J.*, 2021, **27**, 12019–12031.
- M. J. Jellen, I. Liepuoniute, M. Jin, C. G. Jones, S. Yang, X. Jiang, H. M. Nelson, K. N. Houk and M. A. Garcia-Garibay, Enhanced gearing fidelity achieved through macrocyclization of a solvated molecular spur gear, *J. Am. Chem. Soc.*, 2021, **143**, 7740–7747.



- 25 H. Wang, Q. Guan and X. Wang, Theoretical research of covalent and controllable molecular brake based on 9-triptycene, *Theor. Chem. Acc.*, 2021, **140**, 52.
- 26 M. J. Jellen, X. Jiang, S. Benders, A. Adams and M. A. Garcia-Garibay, Slip/stick viscosity models of nanoconfined liquids: solvent-dependent rotation in metal-organic frameworks, *J. Org. Chem.*, 2022, **87**, 1780–1790.
- 27 R. Ushiroguchi, Y. Shuku, R. Suizu and K. Awaga, Variable host-guest charge-transfer interactions in 1D channels formed in a molecule-based honeycomb lattice of phenazine analogue of triptycene, *Cryst. Growth Des.*, 2020, **20**, 7593–7597.
- 28 L. Ueberricke and M. Mastalerz, Triptycene end-capping as strategy in materials chemistry to control crystal packing and increase solubility, *Chem. Rec.*, 2021, **21**, 558–573.
- 29 J. C. Lauer, B. Kohl, F. Braun, F. Rominger and M. Mastalerz, A hexagonal shape-persistent nanobelt of elongated rhombic symmetry with orthogonal π -planes by a one-pot reaction, *Eur. J. Org. Chem.*, 2022, **2022**, e202101317.
- 30 C.-F. Chen and Y. Han, Triptycene-derived macrocyclic arenes: from calixarenes to helicarenes, *Acc. Chem. Res.*, 2018, **51**, 2093–2106.
- 31 S. Hasegawa, S. L. Meichsner, J. J. Holstein, A. Baksi, M. Kasanmascheff and G. H. Clever, Long-lived C_{60} radical anion stabilized inside an electron-deficient coordination cage, *J. Am. Chem. Soc.*, 2021, **143**, 9718–9723.
- 32 M. Holsten, S. Feierabend, S. M. Elbert, F. Rominger, T. Oeser and M. Mastalerz, Soluble congeners of prior insoluble shape-persistent imine cages, *Chem.-Eur. J.*, 2021, **27**, 9383–9390.
- 33 K. Kajiyama, E. Tsurumaki, K. Wakamatsu, G. Fukuhara and S. Toyota, Complexation of an anthracene-triptycene nanocage host with fullerene guests through $CH\cdots\pi$ contacts, *ChemPlusChem*, 2021, **86**, 716–722.
- 34 K. Kawasumi, T. Wu, T. Zhu, H. S. Chae, T. Van Voorhis, M. A. Baldo and T. M. Swager, Thermally activated delayed fluorescence materials based on homoconjugation effect of donor-acceptor triptycenes, *J. Am. Chem. Soc.*, 2015, **137**, 11908–11911.
- 35 S. R. Peurifoy, E. Castro, F. Liu, X. Y. Zhu, F. Ng, S. Jockusch, M. L. Steigerwald, L. Echegoyen, C. Nuckolls and T. J. Sisto, Three-dimensional graphene nanostructures, *J. Am. Chem. Soc.*, 2018, **140**, 9341–9345.
- 36 Q. Liu, X. Chen, Z. Zhou, T. Huang, Y. Wang, S. Xie, Z. Zeng and B. Z. Tang, Spiro-fused bicyclo[3,2,2] octatriene-cored triptycene: synthesis, molecular packing, and functional aggregates, *Sci. China: Chem.*, 2021, **64**, 1976–1984.
- 37 Y. Duan, G. Zhang, X. Liu, F. Shi, T. Wang, H. Yan, H. Xu and L. Zhang, Acene-extended triptycenes: synthesis, characterization, and singlet exciton fission properties, *J. Org. Chem.*, 2022, **87**, 8841–8848.
- 38 H. Langhals, C. Dietl and P. Mayer, FRET in orthogonal, increasingly strain-rigidified systems, *Isr. J. Chem.*, 2022, **62**, e202100021.
- 39 J.-R. Mistry, S. Montanaro and I. A. Wright, Homoconjugation effects in triptycene based organic optoelectronic materials, *Mater. Adv.*, 2023, **4**, 787–803.
- 40 Z.-Y. Tao, Z.-H. Pan, Y.-J. Wang, J. Zhang, Q.-S. Wang, Q.-F. Zhang, B.-H. Tong, M.-K. Fung and H. Kong, Molecular engineering with triptycene groups endows homoleptic Ir(III) complexes with enhanced electroluminescence properties, *Inorg. Chem. Front.*, 2023, **10**, 49–60.
- 41 S. Das, G. Nascimbeni, R. O. de la Morena, F. Ishiwari, Y. Shoji, T. Fukushima, M. Buck, E. Zojer and M. Zharnikov, Porous honeycomb self-assembled monolayers: tripodal adsorption and hidden chirality of carboxylate anchored triptycenes on Ag, *ACS Nano*, 2021, **15**, 11168–11179.
- 42 L. Grossmann, E. Ringel, A. Rastgoo-Lahrood, B. T. King, J. Rosen, W. M. Heckl, D. Opris, J. Björk and M. Lackinger, Steering self-assembly of three-dimensional triptycenes on Au(111) by Tuning Molecule-Surface Interactions, *Angew. Chem., Int. Ed.*, 2022, **61**, e202201044.
- 43 E. Kaletová, C. S. Hurtado, I. Cisařová, S. J. Teat and J. Kaleta, Triptycene-based molecular rods for Langmuir-Blodgett monolayers, *ChemPlusChem*, 2022, **87**, e202200023.
- 44 S. Das, F. Ishiwari, Y. Shoji, T. Fukushima and M. Zharnikov, Triptycene-based self-assembled monolayer as a template for successive click reactions, *J. Phys. Chem. C*, 2023, **127**, 5178–5185.
- 45 S. Das, F. Ishiwari, Y. Shoji, T. Fukushima and M. Zharnikov, Triptycene-based tripodal self-assembled monolayer on indium tin oxide, *Nachr. Chem., Tech. Lab.*, 2023, **127**, 2088–2097.
- 46 F. K.-C. Leung, F. Ishiwari, Y. Shoji, T. Nishikawa, R. Takeda, Y. Nagata, M. Sugimoto, Y. Uozumi, Y. M. A. Yamada and T. Fukushima, Synthesis and catalytic applications of a triptycene-based monophosphine ligand for palladium-mediated organic transformations, *ACS Omega*, 2017, **2**, 1930–1937.
- 47 V. A. Kirkina, G. A. Silantyev, S. De-Botton, O. A. Filippov, E. M. Titova, A. A. Pavlov, N. V. Belkova, L. M. Epstein, D. Gelman and E. S. Shubina, Stereoisomerism as an origin of different reactivities of Ir(III) PC(sp₃)P pincer catalysts, *Inorg. Chem.*, 2020, **59**, 11962–11975.
- 48 I. Kiselev and D. Gelman, Synthesis of rigid chiral C₃-symmetric triptycene-based ligands and their application in enantioselective Cu(I)-catalyzed aziridination of chalcones, *J. Organomet. Chem.*, 2021, **941**, 121804.
- 49 P. S. Kulyabin, G. P. Goryunov, M. I. Sharikov, V. V. Izmer, A. Vittoria, P. H. M. Budzelaar, V. Busico, A. Z. Voskoboinikov, C. Ehm, R. Cipullo and D. V. Uborsky, Ansa-zirconocene catalysts for isotactic-selective propene polymerization at high temperature: a long story finds a happy ending, *J. Am. Chem. Soc.*, 2021, **143**, 7641–7647.
- 50 J. Yu, D. Zhang and Q. Wang, Rigid Triptycene-based di- and trinuclear salicylaldehyde nickel cooperative



- polymerization catalysts, *Organometallics*, 2023, **42**, 307–315.
- 51 D. J. Murray, D. D. Patterson, P. Payamyar, R. Bhola, W. Song, M. Lackinger, A. D. Schlüter and B. T. King, Large area synthesis of a nanoporous two-dimensional polymer at the air/water interface, *J. Am. Chem. Soc.*, 2015, **137**, 3450–3453.
 - 52 V. Müller, A. Hinaut, M. Moradi, M. Baljovic, T. A. Jung, P. Shahgaldian, H. Möhwald, G. Hofer, M. Kröger, B. T. King, E. Meyer, T. Glatzel and A. D. Schlüter, A two-dimensional polymer synthesized at the air/water interface, *Angew. Chem., Int. Ed.*, 2018, **57**, 10584–10588.
 - 53 C. Zhao, L. Chen, Y. Che, Z. Pang, X. Wu, Y. Lu, H. Liu, G. M. Day and A. I. Cooper, Digital navigation of energy–structure–function maps for hydrogen-bonded porous molecular crystals, *Nat. Commun.*, 2021, **12**, 817.
 - 54 B. J. Eckstein, L. C. Brown, B. C. Noll, M. P. Moghadasnia, G. J. Balaich and C. M. McGuirk, A porous chalcogen-bonded organic framework, *J. Am. Chem. Soc.*, 2021, **143**, 20207–20215.
 - 55 K. Koner, S. Karak, S. Kandambeth, S. Karak, N. Thomas, L. Leanza, C. Perego, L. Pesce, R. Capelli, M. Moun, M. Bhakar, T. G. Ajithkumar, G. M. Pavan and R. Banerjee, Porous covalent organic nanotubes and their assembly in loops and toroids, *Nat. Chem.*, 2022, **14**, 507–514.
 - 56 H. Li, J. Ding, X. Guan, F. Chen, C. Li, L. Zhu, M. Xue, D. Yuan, V. Valtchev, Y. Yan, S. Qiu and Q. Fang, Three-dimensional large-pore covalent organic framework with stp topology, *J. Am. Chem. Soc.*, 2020, **142**, 13334–13338.
 - 57 C. Yu, H. Li, Y. Wang, J. Suo, X. Guan, R. Wang, V. Valtchev, Y. Yan, S. Qiu and Q. Fang, Three-dimensional triptycene-functionalized covalent organic frameworks with hea net for hydrogen adsorption, *Angew. Chem., Int. Ed.*, 2022, **61**, e202117101.
 - 58 Y. Zhao, S. Das, T. Sekine, H. Mabuchi, T. Irie, J. Sakai, D. Wen, W. Zhu, T. Ben and Y. Negishi, Record ultralarge-pores, low density three-dimensional covalent organic framework for controlled drug delivery, *Angew. Chem., Int. Ed.*, 2023, **62**, e202300172.
 - 59 J. Lv, W. Li, J. Li, Z. Zhu, A. Dong, H. Lv, P. Li and B. Wang, A triptycene-based 2D MOF with vertically extended structure for improving the electrocatalytic performance of CO₂ to methane, *Angew. Chem., Int. Ed.*, 2023, **62**, e202217958.
 - 60 B. S. Ghanem, K. J. Msayib, N. B. McKeown, K. D. M. Harris, Z. Pan, P. M. Budd, A. Butler, J. Selbie, D. Book and A. Walton, A triptycene-based polymer of intrinsic microporosity that displays enhanced surface area and hydrogen adsorption, *Chem. Commun.*, 2007, 67–69.
 - 61 B. S. Ghanem, M. Hashem, K. D. M. Harris, K. J. Msayib, M. Xu, P. M. Budd, N. Chaukura, D. Book, S. Tedds, A. Walton and N. B. McKeown, Triptycene-based polymers of intrinsic microporosity: organic materials that can be tailored for gas adsorption, *Macromolecules*, 2010, **43**, 5287–5294.
 - 62 N. B. McKeown, Polymers of Intrinsic Microporosity (PIMs), *Polymer*, 2020, **202**, 122736.
 - 63 N. B. McKeown, The structure-property relationships of Polymers of Intrinsic Microporosity (PIMs), *Curr. Opin. Chem. Eng.*, 2022, **36**, 100785.
 - 64 Q.-P. Zhang, Z. Wang, Z.-W. Zhang, T.-L. Zhai, J.-J. Chen, H. Ma, B. Tan and C. Zhang, Triptycene-based chiral porous polyimides for enantioselective membrane separation, *Angew. Chem., Int. Ed.*, 2021, **60**, 12781–12785.
 - 65 B. S. Ghanem, R. Swaidan, E. Litwiller and I. Pinnau, Ultramicroporous triptycene-based polyimide membranes for high-performance gas separation, *Adv. Mater.*, 2014, **26**, 3688–3692.
 - 66 R. Swaidan, M. Al-Saedi, B. Ghanem, E. Litwiller and I. Pinnau, Rational design of intrinsically ultramicroporous polyimides containing bridgehead-substituted triptycene for highly selective and permeable gas separation membranes, *Macromolecules*, 2014, **47**, 5104–5114.
 - 67 J. R. Wiegand, Z. P. Smith, Q. Liu, C. T. Patterson, B. D. Freeman and R. L. Guo, Synthesis and characterization of triptycene-based polyimides with tunable high fractional free volume for gas separation membranes, *J. Mater. Chem. A*, 2014, **2**, 13309–13320.
 - 68 J. R. Weidman and R. L. Guo, The use of iptycenes in rational macromolecular design for gas separation membrane applications, *Ind. Eng. Chem. Res.*, 2017, **56**, 4220–4236.
 - 69 T. Zhang, L. Deng and P. Li, Decarboxylation cross-linking of triptycene-based Tröger's base polymers for gas separation, *Ind. Eng. Chem. Res.*, 2020, **59**, 18640–18648.
 - 70 X. Ma, Z. Zhu, W. Shi, W. Ji, J. Li, Y. Wang and I. Pinnau, Unprecedented gas separation performance of a difluoro-functionalized triptycene-based ladder PIM membrane at low temperature, *J. Mater. Chem. A*, 2021, **9**, 5404–5414.
 - 71 B. S. Ghanem, A facile synthesis of a novel triptycene-containing A-B monomer: precursor to polymers of intrinsic microporosity, *Polym. Chem.*, 2012, **3**, 96–98.
 - 72 A. Fuoco, B. Comesana-Gandara, M. Longo, E. Esposito, M. Monteleone, I. Rose, C. G. Bezzu, M. Carta, N. B. McKeown and J. C. Jansen, Temperature dependence of gas permeation and diffusion in triptycene-based ultrapermeable Polymers of Intrinsic Microporosity, *ACS Appl. Mater. Interfaces*, 2018, **10**, 36475–36482.
 - 73 T. M. Long and T. M. Swager, Minimization of free volume: alignment of triptycenes in liquid crystals and stretched polymers, *Adv. Mater.*, 2001, **13**, 601–604.
 - 74 I. Rose, M. Carta, R. Malpass-Evans, M.-C. Ferrari, P. Bernardo, G. Clarizia, J. C. Jansen and N. B. McKeown, Highly permeable benzotriptycene-based polymer of intrinsic microporosity, *ACS Macro Lett.*, 2015, **4**, 912–915.
 - 75 I. Rose, C. G. Bezzu, M. Carta, B. Comesana-Gándara, E. Lasseguette, M. C. Ferrari, P. Bernardo, G. Clarizia, A. Fuoco, J. C. Jansen, K. E. Hart, T. P. Liyana-Arachchi, C. M. Colina and N. B. McKeown, Polymer ultrapermeability from the inefficient packing of 2D chains, *Nat. Mater.*, 2017, **16**, 932–937.



- 76 M. Carta, M. Croad, R. Malpass-Evans, J. C. Jansen, P. Bernardo, G. Clarizia, K. Friess, M. Lanc and N. B. McKeown, Triptycene induced enhancement of membrane gas selectivity for microporous Troger's base polymers, *Adv. Mater.*, 2014, **26**, 3526–3531.
- 77 R. Swaidan, B. Ghanem and I. Pinnau, Fine-tuned intrinsically ultramicroporous polymers redefine the permeability/selectivity upper bounds of membrane-based air and hydrogen separations, *ACS Macro Lett.*, 2015, **4**, 947–951.
- 78 B. Comesaña-Gándara, J. Chen, C. G. Bezzu, M. Carta, I. Rose, M.-C. Ferrari, E. Esposito, A. Fuoco, J. C. Jansen and N. B. McKeown, Redefining the Robeson upper bounds for CO₂/CH₄ and CO₂/N₂ separations using a series of ultrapermeable benzotriptycene-based polymers of intrinsic microporosity, *Energy Environ. Sci.*, 2019, **12**, 2733–2740.
- 79 Y. Jiang and C.-F. Chen, Recent developments in synthesis and applications of triptycene and pentiptycene derivatives, *Eur. J. Org. Chem.*, 2011, **2011**, 6377–6403.
- 80 Y.-X. Ma, Z. Meng and C.-F. Chen, Synthesis of substituted iptycenes, *Synlett*, 2015, **26**, 6–30.
- 81 M. S. Taylor and T. M. Swager, Triptycenediols by rhodium-catalyzed [2 + 2 + 2] cycloaddition, *Org. Lett.*, 2007, **9**, 3695–3697.
- 82 Y. Aida, Y. Shibata and K. Tanaka, Enantioselective synthesis of distorted π -extended chiral triptycenes consisting of three distinct aromatic rings by rhodium-catalyzed [2+2+2] cycloaddition, *Chem.–Eur. J.*, 2020, **26**, 3004–3009.
- 83 B. VanVeller, D. Robinson and T. M. Swager, Triptycene diols: a strategy for synthesizing planar π systems through catalytic conversion of a poly(p-phenylene ethynylene) into a poly(p-phenylene vinylene), *Angew. Chem., Int. Ed.*, 2012, **51**, 1182–1186.
- 84 S. Umez, G. d. P. Gomes, T. Yoshinaga, M. Sakae, K. Matsumoto, T. Iwata, I. Alabugin and M. Shindo, Regioselective One-Pot Synthesis of triptycenes via triple-cycloadditions of arynes to ynolates, *Angew. Chem., Int. Ed.*, 2017, **56**, 1298–1302.
- 85 T. Yoshinaga, T. Fujiwara, T. Iwata and M. Shindo, Synthesis of distorted 1,8,13-trisilyl-9-hydroxytriptycenes by triple cycloaddition of ynolates to 3-silylbenzynes, *Chem.–Eur. J.*, 2019, **25**, 13855–13859.
- 86 G. Wittig and R. Ludwig, Triptycen aus anthracen und dehydrobenzol, *Angew. Chem.*, 1956, **68**, 40.
- 87 Y. Ryu, C.-S. Hyun and B.-K. An, Practical synthesis of triptycene trisquinone, *Synth. Commun.*, 2022, **52**, 1184–1189.
- 88 T. F. Mich, E. J. Nienhou, T. E. Farina and J. J. Tufariel, Generation of benzyne – a warning, *J. Chem. Educ.*, 1968, **45**, 272.
- 89 L. Friedman and F. M. Logullo, Benzynes via aprotic diazotization of anthranilic acids: a convenient synthesis of triptycene and derivatives, *J. Am. Chem. Soc.*, 1963, **85**, 1549.
- 90 G. K. S. Prakash, C. Panja, A. Shakhmin, E. Shah, T. Mathew and G. A. Olah, BF₃–H₂O catalyzed hydroxyalkylation of aromatics with aromatic aldehydes and dicarboxaldehydes: efficient synthesis of triarylmethanes, diarylmethylbenzaldehydes, and anthracene Derivatives, *J. Org. Chem.*, 2009, **74**, 8659–8668.
- 91 J. B. Niederl and H. J. Vogel, Aldehyde–resorcinol condensations, *J. Am. Chem. Soc.*, 1940, **62**, 2512–2514.
- 92 E. Dalcanele, P. Soncini, G. Bacchilega and F. Uguzzoli, Selective complexation of neutral molecules in organic solvents. Host–guest complexes and cavities between cavitands and aromatic compounds, *J. Chem. Soc., Chem. Commun.*, 1989, 500–502.
- 93 P. Timmerman, W. Verboom and D. N. Reinhoudt, Resorcinarenes, *Tetrahedron*, 1996, **52**, 2663–2704.
- 94 G. Li, S. Zhou, G. Su, Y. Liu and P. G. Wang, Improved synthesis of aryl-substituted anthracenes and heteroacenes, *J. Org. Chem.*, 2007, **72**, 9830–9833.
- 95 J. A. Clement, R. Sivasakthikumar, A. K. Mohanakrishnan, S. Sundaramoorthy and D. Velmurugan, Lewis-acid-mediated domino reactions of bis(diacetoxymethyl)-substituted arenes and heteroarenes, *Eur. J. Org. Chem.*, 2011, **2011**, 569–577.
- 96 R. Sivasakthikumar, S. M. Rafiq, E. Sankar, J. A. Clement and A. K. Mohanakrishnan, Regioselective annulation of unsymmetrical 1,2-phenylenebis(diaryl/diheteroarylmethanol): a facile synthesis of anthracene, tetracene, and naphtho[b]thiophene analogues, *Eur. J. Org. Chem.*, 2015, **2015**, 7816–7835.
- 97 K. Mohammadiannejad-Abbasabadi, I. Mohammadpoor-Baltork, S. Tangestaninejad, M. Moghadam, V. Mirkhani and R. Kia, Bi(OTf)₃-catalysed domino Friedel–Crafts alkylation of arenes with aldehydes: an upgraded method for efficient synthesis of triarylmethanes and anthracene derivatives, *Tetrahedron*, 2016, **72**, 1433–1439.
- 98 J. P. Kass, L. A. Slasor, C. H. Zambrano and E. E. Dueño, Improved synthesis and purification of cavitands, *Org. Prep. Proced. Int.*, 2006, **38**, 480–483.
- 99 H. Ito, T. Nakayama, M. Sherwood, D. Miller and M. Ueda, Characterization and lithographic application of calix[4]resorcinarene derivatives, *Chem. Mater.*, 2008, **20**, 341–356.
- 100 A. J. Lacher, PhD thesis, *Conformational analysis of some 7-substituted-7,12-dihydropleiadenes*, University of Buffalo, 1967. See footnote 9 in ref. 101.
- 101 P. T. Lansbury, J. B. Bieber, F. D. Saeva and K. R. Fountain, 7,12-Dihydropleiadenes. VIII. Transannular 1,5 hydride shift accompanying synthesis of 7-alkyl-1,12-(o-phenylene)-7,12-dihydropleiadenes by cyclodehydration, *J. Am. Chem. Soc.*, 1969, **91**, 399–405.
- 102 L. F. Fieser and M. Fieser, Condensation and ring closures in the naphthalene series. V. Synthesis of phthaloylnaphthol, *J. Am. Chem. Soc.*, 1933, **55**, 3010.
- 103 M. P. Cava and R. H. Schlessinger, Reactive o-quinonoid aromatic hydrocarbons of the pleiadene series, *J. Am. Chem. Soc.*, 1963, **85**, 835–836.
- 104 IUPAC, Definitive rules for nomenclature of organic chemistry, *J. Am. Chem. Soc.*, 1960, **82**, 5545–5574.



- 105 B. M. Babu, P. B. Thakur, N. N. Rao, G. S. Kumar and H. M. Meshram, A rapid, highly efficient, and general protocol for the synthesis of functionalized triarylmethanes: a straightforward access for the synthesis of (–)-tatarinoid C, *Tetrahedron Lett.*, 2014, **55**, 1868–1872.
- 106 J. R. Moran, S. Karbach and D. J. Cram, Cavitands: synthetic molecular vessels, *J. Am. Chem. Soc.*, 1982, **104**, 5826–5828.
- 107 J. R. Moran, J. L. Ericson, E. Dalcanale, J. A. Bryant, C. B. Knobler and D. J. Cram, Vases and kites as cavitands, *J. Am. Chem. Soc.*, 1991, **113**, 5707–5714.
- 108 P. M. Budd, B. Ghanem, K. Msayib, N. B. McKeown and C. Tattershall, A nanoporous network polymer derived from hexaazatrinaphthylene with potential as an adsorbent and catalyst support, *J. Mater. Chem.*, 2003, **13**, 2721–2726.
- 109 M. Heuchel, D. Fritsch, P. M. Budd, N. B. McKeown and D. Hofmann, Atomistic packing model and free volume distribution of a polymer with intrinsic microporosity (PIM-1), *J. Membr. Sci.*, 2008, **318**, 84–99.
- 110 L. P. Skala, A. Yang, M. J. Klemes, L. Xiao and W. R. Dichtel, Resorcinarene cavitand polymers for the remediation of halomethanes and 1,4-dioxane, *J. Am. Chem. Soc.*, 2019, **141**, 13315–13319.
- 111 N. Ogawa, Y. Yamaoka, K.-i. Yamada and K. Takasu, Synthesis of π -extended fluoranthenes via a KHMDS-promoted anionic-radical reaction cascade, *Org. Lett.*, 2017, **19**, 3327–3330.
- 112 S. Norvez, Liquid crystalline triptycene derivatives, *J. Org. Chem.*, 1993, **58**, 2414–2418.
- 113 N. Seiki, Y. Shoji, T. Kajitani, F. Ishiwari, A. Kosaka, T. Hikima, M. Takata, T. Someya and T. Fukushima, Rational synthesis of organic thin films with exceptional long-range structural integrity, *Science*, 2015, **348**, 1122–1126.
- 114 Y. Li, R. Cao and S. J. Lippard, Design and synthesis of a novel triptycene-based ligand for modeling carboxylate-bridged diiron enzyme active sites, *Org. Lett.*, 2011, **13**, 5052–5055.
- 115 F. Ishiwari, G. Okabe, T. Kajitani and T. Fukushima, Introduction of triptycene with a particular substitution pattern into polymer chains can dramatically improve the structural and rheological properties, *ACS Macro Lett.*, 2021, **10**, 1529–1534.
- 116 R. Kavitha and T. Stalin, Naphthalenediols: a new class of novel fluorescent chemosensors for selective sensing of Cu^{2+} and Ni^{2+} in aqueous solution, *J. Lumin.*, 2015, **158**, 313–321.

