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Functionalization of pillar[*n*]arenes towards optically responsive systems *via* host–guest interactions

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Because of their host–guest complexation ability, pillar[*n*]arenes are promising building blocks for optically responsive materials. The ease of introducing functional groups into pillar[*n*]arenes allows for versatile molecular design. Moreover, the guest selectivity, donor properties, and planar chirality of pillar[*n*]arenes enable creation of unique response systems. This review presents progress in the field of pillar[*n*]arene-based optical response systems, focusing on color, fluorescence, circular dichroism, and circularly polarized luminescence signal changes *via* host–guest interactions in solution and solid states.

1. Introduction

The development of cyclic host molecules such as cyclodextrins,[1–4] cucurbit[*n*]urils,[5–8] crown ethers,[9] and calix[*n*]arenes[10–13] has greatly advanced the field of supramolecular chemistry. One of the most important features of cyclic host molecules is their ability to recognize guest molecules inside the cavity. This property allows for their application as optically responsive materials,[14–21] catalysts,[22–25] supramolecular polymers,[26–29] and molecular machines.[30–34] Optically responsive materials can be synthesized by simply introducing substituents with optical properties. The optical response occurs because of a structural change caused by host–guest complexation. Therefore, creating optically responsive materials using cyclic host molecules as scaffolds is an effective strategy.

Pillar[*n*]arenes are a relatively new class of cyclic host molecules that were reported in 2008 by our groups.[35–38] Because 1,4-dialkoxybenzene units are connected by a methylene bridge at the *para*-position, pillar[*n*]arenes have a symmetrical pillar-shaped structure (Fig. 1a). Over the past 15 years, many studies of pillar[*n*]arene-based optically responsive materials have been reported.[16] Compared with other cyclic host molecules, the use of pillar[*n*]arenes as scaffolds offers the following advantages for preparation of optically responsive materials.

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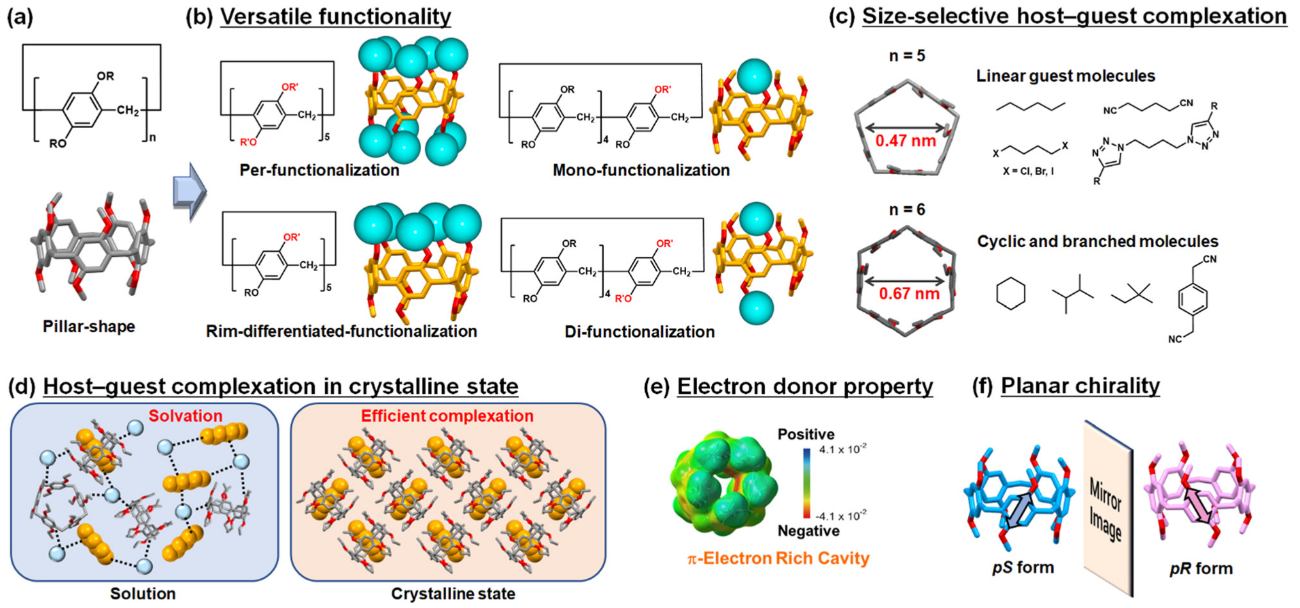

Fig. 1 (a) Chemical and crystallographic structure of pillar[*n*]arene. (b) Versatile functionality of pillar[*n*]arene. (c) Cavity sizes of pillar[5]arene and pillar[6]arene, and suitable guest molecules for pillar[5]arene and pillar[6]arene. (d) Host–guest complexation events in solution and crystalline states. (e) Electrostatic potential profile of perethylated pillar[5]arene. (f) Planar chirality of pillar[*n*]arene.

1. Versatile functionality: research by pillar[*n*]arene chemists has led to the development of versatile functionalization approaches for pillar[*n*]arenes (Fig. 1b).[39–41] One useful approach is post modification after cyclization. Oxidation followed by reduction of 1,4-dialkoxy benzene[42,43] or deprotection of alkoxy groups[35,44,45] can yield phenolic groups with high reactivity. Another approach is co-cyclization with different 1,4-dialkoxybenzene monomers[46,47] or pre-oriented cyclization with asymmetrically substituted 2,5-dialkoxybenzyl alcohols.[48–50] These synthetic approaches allow access to per-, mono-, and di-functionalized and rim-differentiated pillar[*n*]arenes. Because of this high versatility, optically responsive groups can be easily installed at desired positions to develop optically responsive materials.

2. Size-selective guest inclusion: by means of C–H/π interactions, pillar[*n*]arenes can take up various guest molecules with C–H groups.[51–53] This uptake of guest molecules shows size selectivity depending on the ring size of the pillar[*n*]arene (Fig. 1c). Pillar[5]arene has a cavity (*ca.* 0.47 nm) that is suitable for encapsulation of linear guest molecules.[54,55] Compared with pillar[5]arene, pillar[6]arene has a larger cavity (*ca.* 0.67 nm) and can accommodate cyclic and branched guest molecules.[56,57] The ring size of the pillar[*n*]arene can be selected according to the target guest molecules when creating the optically responsive materials.

3. Host–guest complexation in a crystalline state: recognition of guest molecules by cyclic host molecules has mainly been investigated in solution. Host–guest complexation in solution is greatly affected by solvation because of the numerous solvent molecules, which would inhibit efficient complexation in some cases (Fig. 1d). To solve the solvation problem, in 2015, our group reported efficient uptake of guest vapor molecules by pillar[5]arene crystals.[55] In the crystalline state, quantitative guest molecule incorporation occurs without the influence of solvation. One of the key features is crystal structural change as vapor molecules are taken up.[58,59] The preparation of optically responsive materials using this crystal structural change before and after vapor molecule uptake is also discussed in this review (Section 3).

4. Electron donor properties: charge-transfer (CT) interactions between a donor and acceptor are useful for preparation of optically responsive materials.[60–64] Because the substituent of the pillar[*n*]arene consists of electron-rich 1,4-dialkoxybenzene, pillar[*n*]arene acts as a donor (Fig. 1e).[60,65,66] Co-crystallization with acceptor molecules is a simple method to form CT complexes, and optically responsive materials can be created by host–guest complexation in the crystalline state. Another useful method is the covalent introduction of an acceptor group directly into the pillar[*n*]arene, which also takes advantage of intramolecular CT interactions.

5. Planar chirality: because of the position of the substituent groups in the benzene units, pillar[5]arene exhibits planar chirality (*pS* and *pR* forms, Fig. 1f).[67–70] Chiroptical properties, such as circular dichroism (CD) and circularly polarized luminescence (CPL), that arise because of this planar chirality have been studied. Furthermore, interconversion between *pS* and *pR* forms occurs because of rotation of benzene units.[71–74] Therefore, switching materials with chiroptical properties can be developed using this interconversion of planar chirality. Cyclic host molecules with such dynamic planar chirality are rare, allowing for the development of unique optically responsive materials based on dynamic planar chirality of pillar[*n*]arenes.

In this review, we focus on optically responsive materials prepared by substitution of pillar[*n*]arenes. First, we discuss the fluorescence responses in solution systems. We also introduce the CD and CPL signal responses, which are specific properties of pillar[*n*]arenes. Second, the optical responses in the solid state (*i.e.*, color and emission changes), which are well developed compared with other cyclic molecules, are also discussed.

2. Optically responsive systems *via* host–guest interactions in solution

Optically responsive systems prepared from various cyclic host molecules have mainly been studied in solution. One of the strategies to change the optical properties in solution is to induce a conformational change in the host molecules. Pillar[*n*]arenes have flexible structures because they contain sp^3 carbon atoms in methylene bridges, which can allow for conformational changes.[68,75–78] In this section, we present the fluorescence, CD, and CPL signal responses resulting from structural changes of pillar[*n*]arenes. Other ways to achieve optical responses are to trigger photo-induced electron transfer (PET) and energy transfer (ET) through interactions between the host and guest molecules.[79–84] These strategies are also discussed in this section.

2.1 Fluorescence responsive systems

The introduction of fluorophores into pillar[5]arenes provides fluorescence responsive systems upon host–guest complexation. In this section, we first discuss pillar[5]arene-based fluorescence-responsive materials prepared by introducing fluorophores using the copper(I)-catalyzed alkyne–azide cycloaddition (CuAAC) click reaction.[41,43,85–87] Stoddart and coworkers found that host–guest complexation occurred between per-methylated pillar[5]arene and aliphatic amines.[46] Pillar[5]arene was considered to act as a sensor for the aliphatic amines. Pillar[5]arene **H1** with a mono-pyrene group was prepared *via* CuAAC click reactions, and represents the first mono-fluorophore-functionalized pillar[5]arene (Fig. 2a). **H1** maintained the ability of per-methylated pillar[5]arenes to take up aliphatic amines and exhibited a high association constant in the order of 10^4 M^{-1} for a 1 : 1 (v/v) ratio of $MeCN/H_2O$. Upon addition of aliphatic amines, fluorescence of compound **H1** was effectively quenched through PET. On the other hand, the fluorescence quenching was not observed in the absence of the pillar[5]arene skeleton or pyrene groups, which indicated that the combination of the pillar[5]arene skeleton and the fluorescence emitter was important.

Kursunlu and coworkers reported a synthesis of pillar[5]arene **H2** bearing per-BODIPY for the selective detection of amino acids (Fig. 2b).[88] **H2** was prepared using the CuAAC click reaction. By adding 13 amino acids, the utility as a chemosensor was investigated in DMF/H_2O (1 : 1, v/v). Among the examined amino acids, only L-asparagine enhanced the fluorescence intensity. The enhancement in the emission intensity could be explained by the selective host–guest complexation with L-asparagine resulting in energy transfer between the conjugated fluorescent fragments through the constructed L-asparagine bridge.

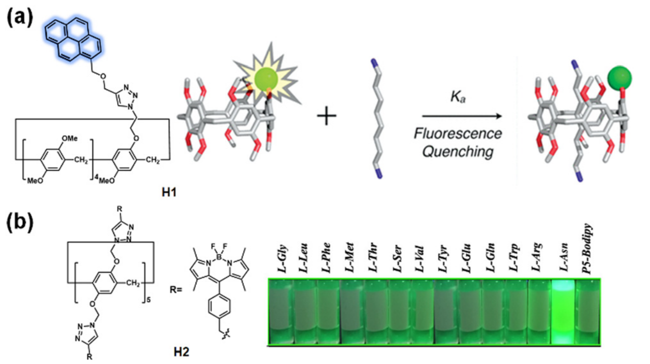

Fig. 2 (a) Fluorescence quenching by PET between **H1** and aliphatic amines. Reproduced with permission from ref. 46 (Copyright 2011 American Chemical Society). (b) Fluorescence enhancement of **H2** for selective detection of L-asparagine from amino acids. Reproduced with permission from ref. 88 (Copyright 2020 Elsevier Inc.).

The incorporation of fluorophores into pillar[*n*]arene cores using the Suzuki–Miyaura coupling reaction is another strategy for creating fluorescence-responsive materials. Although the above examples using the CuAAC click reactions showed that the recognition site and the emissive site played independent roles, the pillar[*n*]arene cores in this strategy worked both as photoresponsive π-conjugated units and recognition sites. Zhu, Zhang, Huang, and coworkers synthesized **H3** which contain donor and acceptor moieties by the Suzuki–Miyaura coupling reactions using ditriflate substituted pillar[5]arene as a precursor (Fig. 3a).[89] **H3** served as a linear donor (triethylamine)–spacer–acceptor (triphenyl acrylonitrile) structure and showed aggregation-induced emission (AIE).[90] Interestingly, **H3** exhibited dual emission with both locally-excited (LE) state emission and intramolecular through-space charge transfer (TSCT) emission. The LE/TSCT dual emission could be controlled by restriction of intramolecular motion. The formation of aggregation states and the increase in solvent viscosity resulted in a decrease in LE emission and an increase in TSCT emission. This change could also be induced by addition of neutral guest molecules such as 1,6-dibromohexane and adiponitrile (**6AN**). Furthermore, white emission could be achieved by adjusting the amount of the guest.

The molecules introduced above showed fluorescence responses with guest recognition but the guest recognition site was located only in the pillar[*n*]arene cavities. By contrast, in the biocatalyst process between an enzyme and substrate, complexation occurs using interactions at multiple sites. To mimic the biocatalyst process, Tang, Cao, and coworkers synthesized **H4** over several steps using Suzuki–Miyaura coupling reactions (Fig. 3b).[91] **H4** can stabilize a complex through multiple interactions because the carboxyl groups at both ends act as interaction sites in addition to the pillar[5]arene cavity. Moreover, because the introduced conjugated moiety contains a quinoline-malononitrile unit, which is an excellent AIE building block, a change in fluorescence intensity can be realized

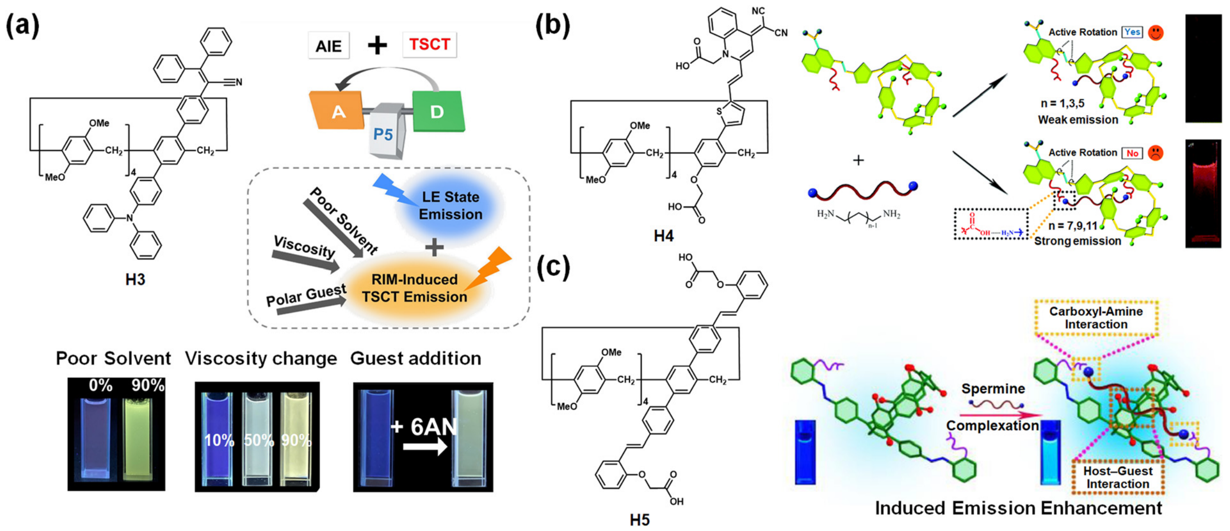

Fig. 3 (a) Chemical structure of **H3** exhibiting dual emission and fluorescence regulation triggered by poor solvent, viscosity change, and guest addition. Reproduced with permission from ref. 89 (Copyright 2022 Wiley-VCH Verlag GmbH & Co. KGaA). Schematic representation of the fluorescence enhancement mechanism using three binding sites of (b) **H4** and (c) **H5** for detection of alkane diamines and spermine, respectively. Reproduced with permission from ref. 91 and 92 (Copyright 2020 Royal Society of Chemistry and 2023 Elsevier Inc.).

because of inhibition of molecular motion. Indeed, **H4** detected alkanediamines with suitable alkyl chain lengths (*i.e.*, 1,12-diaminododecane, 1,10-diaminodecane, and 1,8-diaminooctane) and produced a dramatic increase in fluorescence intensity. This enhancement of fluorescence intensity was attributed to the induced-fit mechanism caused by alkanediamine recognition of **H4**, which resulted in inhibition of the molecular rotation. On the other hand, ethylenediamine, 1,4-butanediamine, and 1,6-hexanediamine could not be detected because the alkyl chain length was not sufficient to reach binding sites of the carboxyl groups.

The same group synthesized **H5** to detect spermine, which is a type of biogenic amine (Fig. 3c).[92] Because of the correlation between elevated levels of spermine and the presence of cancer, detection of spermine is critical for early detection and evaluation of the efficacy of cancer treatment. **H5** can strongly capture spermine because it has three binding sites: two carboxyl groups, and a pillar[5]arene cavity. Spermine was successfully detected through an increase in the fluorescence intensity of **H5.** The increase in fluorescence intensity was attributed to the inhibition of free rotation of fluorophores *via* host–guest complexation. The limit of detection for spermine in acetonitrile was 0.094 ± 0.002 μmol L^{-1}, which indicated that **H5** was a highly sensitive probe for spermine.

Pre-organized pseudorotaxane structures are also promising platforms for creation of stimuli-responsive materials because of their reversible host–guest abilities.[34,93–103] Yang, Wang, and coworkers fabricated pseudo[5]rotaxane between monosulfonic pillar[5]arene **H6** and a neutral guest with a tetraphenylethene core, and found that **H6** exhibited AIE (Fig. 4a).[104] Strong emission in a dilute solution was observed from the pseudo[5]rotaxane because of restriction of the intramolecular rotation of phenyl rings of the tetraphenylethene core, which resulted in blocking of the nonradiative emission. The prepared fluorescence complex exhibited responsiveness to multiple stimuli. Ethylenediamine-induced quenching of the fluorescence intensity occurred because of the dissociation of the pseudo[5]rotaxane of **H6** and the tetraphenylethene-based guest. The supramolecular assembly could also be applied as a temperature sensor. An increase in the temperature induced a decrease in the fluorescence intensity because of dissociation of the pseudo[5]rotaxane. After cooling to the initial temperature (room temperature), the original fluorescence intensity was observed because of re-formation of the pseudo[5]rotaxane.

The pseudo[3]rotaxane showing a fluorescence photo-switch property was constructed, by Ma, Cao, Wang and coworkers, with AIE-active pillar[5]arene **H7** bearing tetraphenyl ethylene moieties and a photo-responsive guest based on a bithienylethene (Fig. 4b).[105] Pseudo[3]rotaxane formation restricted the intramolecular rotation of tetraphenyl ethylene moieties on **H7** and enhanced the fluorescence intensity. The bithienylethene unit of the pseudo[3]rotaxane exhibited reversible photoisomerization between the open and closed forms on alternation of ultraviolet (UV) and visible light irradiation. After UV irradiation, fluorescence resonance energy transfer (FRET) occurred from the tetraphenyl ethylene moieties in **H7** to the closed formed bithienylethene unit and this quenched the emission. After visible light irradiation, pseudo[3]rotaxane, which consisted of the open-form isomer of the bithienylethene unit and **H7**, did not show FRET, and the fluorescence emission was enhanced. Consequently, by alternating the UV and visible light irradiation, the fluorescence on/off switching could be controlled with high reversibility.

A multi-responsive [*c*2]daisy chain prepared using ditopic pillar[5]arene was reported by Yang, Zhang, and coworkers (Fig. 4c).[106] Pillar[5]arenes bearing one anthracene moiety (**H8**), and bearing one anthracene moiety and one tertiary ammonium-ended alkyl chain (**H9**) were prepared. The

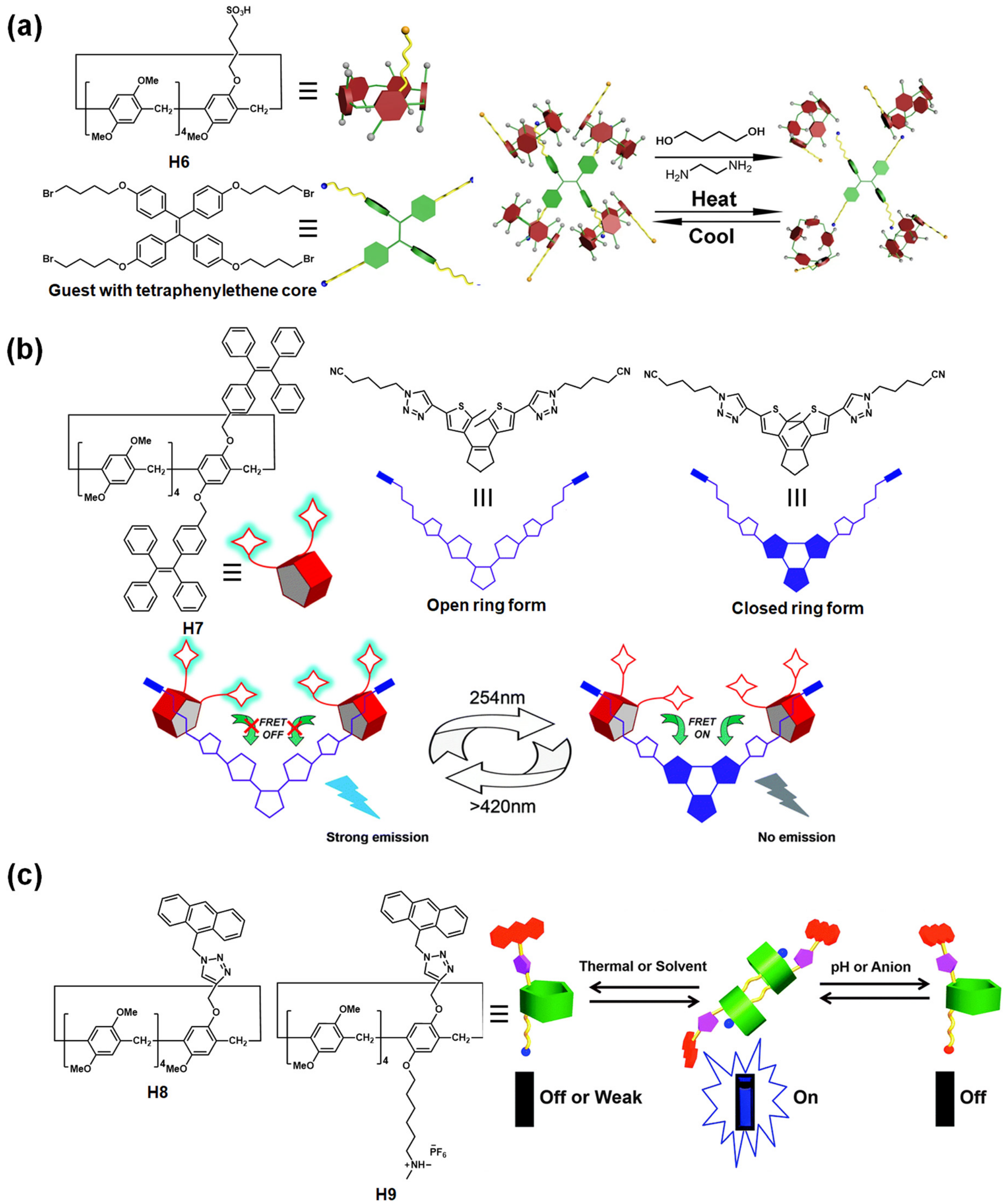

Fig. 4 (a) Schematic representation of the pseudorotaxane formation between **H6** and the tetraphenylethene derivative guest, and its response to stimuli. Reproduced with permission from ref. 104 (copyright 2018 The Author(s) under the terms of the Creative Commons CC BY license). (b) Schematic representation of the photoresponsive fluorescence switching of the pseudo[3]rotaxane between **H7** and bithienylethene derivative guest. Reproduced with permission from ref. 105 (Copyright 2018 Royal Society of Chemistry). (c) Schematic representation of the switching emission of the [c2]daisy chain under different external stimuli. Reproduced with permission from ref. 106 (Copyright 2014 Royal Society of Chemistry).

fluorescence spectra of these molecules were investigated in chloroform. Upon excitation with UV light at 370 nm, **H8** emitted weakly. By contrast, **H9** had strong emission because of the formation of [*c*2]daisy chain. The density functional theory (DFT) calculation of **H8** suggested a mechanism for the enhanced fluorescence intensity. The calculated rotational barriers of the single bond connecting the anthracene moiety were very different in the presence and absence of a tertiary ammonium-terminated alkyl guest. Considering that the [*c*2]daisy of **H9** had a similar threading structure to the complex of **H8** and a tertiary ammonium-ended alkyl guest, the calculated results supported that [*c*2]daisy chain formation of **H9** restricted rotation of the anthracene moiety. Consequently, fluorescence enhancement was observed. The formation and degradation of the [*c*2]daisy chains of **H9** could be induced by changes in the temperature, solvent composition, pH, and counter anions, which would result in the fluorescence switching on and off.

2.2 CD signal responsive systems

The planar chirality of pillar[*n*]arene has a dynamic character. Interconversion between *pS* and *pR* forms occurs by unit rotations.[67,68] Experimental and calculated results show that negative and positive CD signals at 310 nm in the range of π–π* transitions are observed from the *pS* and *pR* forms, respectively.[107–109] Therefore, CD signals can be induced by creating an unequal population of the *pS*/*pR* isomers. One simple method for inducing planar chirality of pillar[*n*]arenes is diastereomeric host–guest complexation by adding chiral guest molecules to a racemic mixture of pillar[*n*]arene (Fig. 5a). This planar chirality induction strategy using a chiral guest was first reported by Yang, Wu, and coworkers in 2020.[110] A series of pillar[5]arenes bearing *n*-alkyl chains of various lengths (**H10–H18**) were prepared and the induced CD signals were investigated by complexation with 16 amino acid derivatives in chloroform (Fig. 5b). Both the handedness and enantiopurity of the chiral amino acid derivative could be determined from the CD signal of the complex. Surprisingly, the CD response changed greatly with changes in the length of the *n*-alkyl chains on the pillar[5]arene rims. Complete inversion of the CD signals was also observed even for the same chiral guest.

Also in 2020, two groups reported induction of planar chirality after addition of chiral guests in aqueous solution. Ma, Lin, Jiang, and coworkers used a water-soluble pillar[5]arene **H19** to capture 19 L/D-amino acid alkyl ester hydrochlorides in aqueous solution, which induced CD signals (Fig. 5c).[111] The *pR* form of **H19** was induced only by L-arginine derivatives and thus showed a positive CD signal at 303 nm. The other 18 L-amino acid derivatives induced *pS* forms and exhibited negative CD signals. This difference in induced CD signals was ascribed to the different binding modes of amino acid alkyl ester hydrochlorides with **H19**. The α-positioned side chain of L-arginine was located inside the **H19** cavity, while that of L-alanine was located outside. Huang, Wang, Hong, and coworkers reported the detection of basic amino acids (*i.e.*, arginine and lysine) by simple mixing with the water-soluble pillar[5,6]arenes **H20** and **H21** (Fig. 5d).[112] With both compounds, D-arginine and L-arginine induced negative and positive cotton effects, respectively. Interestingly, the induced CD signals decreased with heating because high temperatures caused dissociation of the host–guest complex.

Formation of diastereomeric pillar[*n*]arenes by introducing chiral side chains into pillar[*n*]arene scaffolds is another method that generates a bias in the population of planar chirality (*i.e.*, *pS*/*pR* isomers).[113–116] In this system, the host–guest interaction with the achiral guest regulates the planar chirality of pillar[*n*]arenes and causes the CD signal. We demonstrated chiral regulation using a diastereomeric pillar[5]arene bearing ten 2-(*S*)-methylbutoxy groups (**H22**) (Fig. 6a).[117,118] The CD spectra of **H22** changed dramatically when using dihaloalkane guest solvents with different chain lengths. In short-chain guest solvents, such as 1,2-dichloroethane, 1,2-dibromoethane, and 1,3-dibromopropane, **H22** exhibited positive CD signals originating from the *pR* form. By contrast, in longer-chain guest solvents, such as 1,4-dibromobutane, 1,5-dibromopentane, and 1,6-dibromohexane, negative CD signals were observed, which indicated that the *pS* form was favored. The

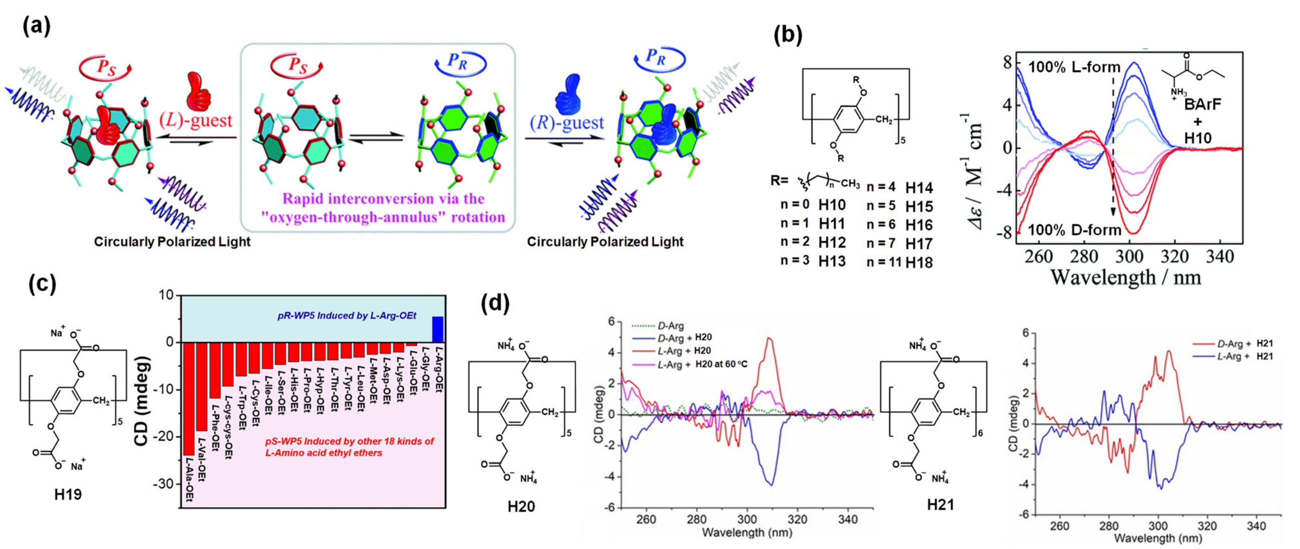

Fig. 5 (a) Schematic representation of the planar chiral regulation by chiral guests. Reproduced with permission from ref. 110 (Copyright 2020 Royal Society of Chemistry). Chemical structures and CD signal responses of (b) **H10–H18**, (c) **H19**, and (d) **H20** and **H21**. Reproduced with permission from ref. 110, 111, and 112 (Copyright 2020 Royal Society of Chemistry, 2020 American Chemical Society, and 2020 Wiley-VCH Verlag GmbH & Co. KGaA).

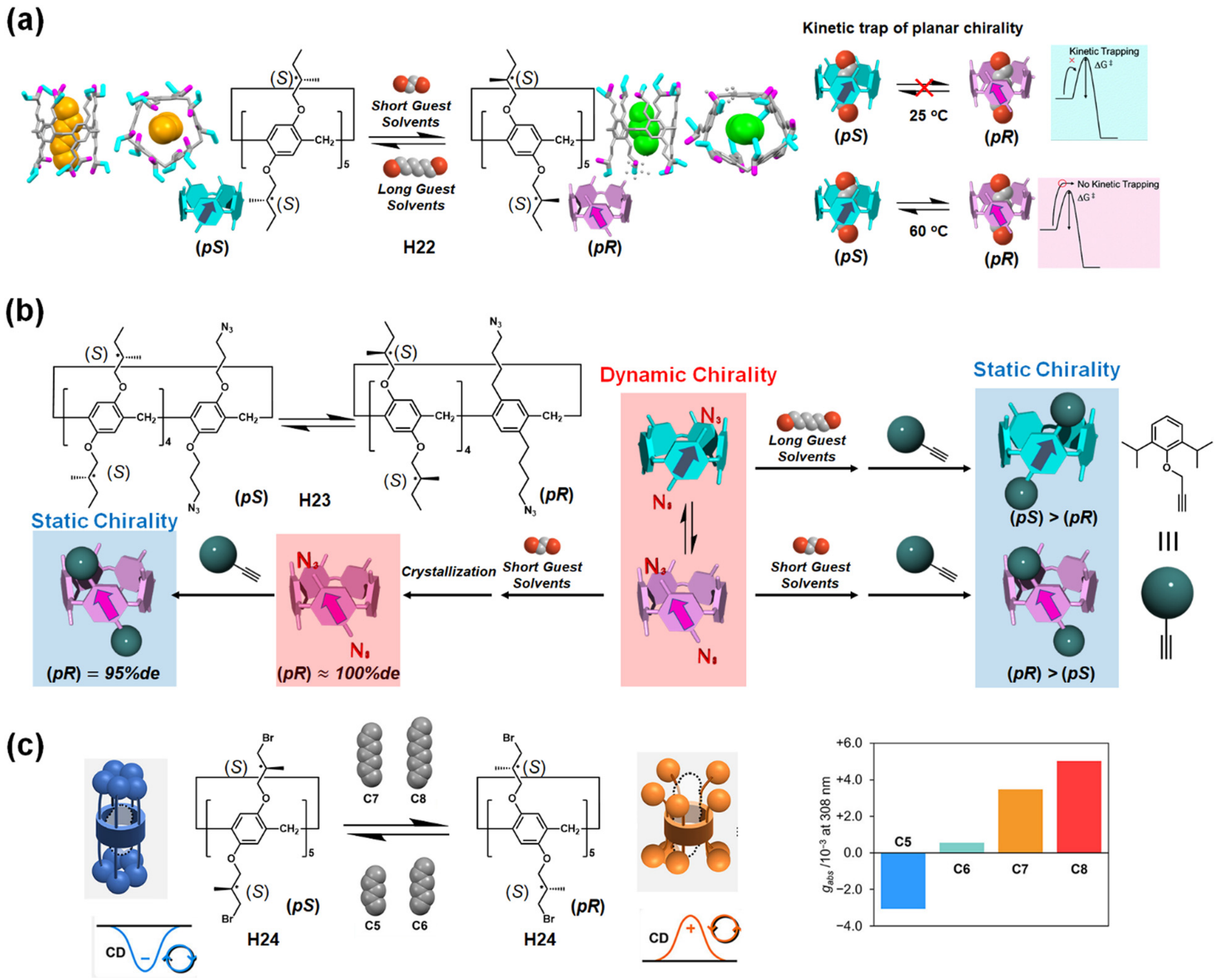

Fig. 6 (a) Chemical structure of diastereomeric pillar[5]arene **H22** and planar chiral inversion and holding by the achiral guest. Reproduced with permission from ref. 118 (Copyright 2020 Royal Society of Chemistry). (b) Schematic representation of the planar chirality regulation and subsequent memory *via* introduction of covalent bonds. Reproduced with permission from ref. 119 (Copyright 2023 Wiley-VCH Verlag GmbH & Co. KGaA). (c) Schematic representation of distinguishing *n*-alkane length with planar-chiral inversion. Reproduced with permission from ref. 120 (Copyright 2023 American Chemical Society).

mechanism of the regulation of the planar chirality was revealed using single crystal X-ray structures. When the guest length was short, the ethyl branch of the side chain filled the inner cavity, which induced the *pR* form. By contrast, when longer guest molecules were used, the ethyl side chain was located outside the cavity because of steric hindrance, which induced the *pS* form. Interestingly, regulated planar chirality could be trapped by inclusion of guest solvents with strong binding affinity to **H22**. However, this kinetic trap of planar chirality worked at 25 °C but not at 60 °C, that is, the kinetic trap through host–guest complexation did not provide perfect memorization because of the non-covalent interaction. The introduction of bulky substituents by covalent bonding is an alternative method for fixing the planar chirality because exchange between the *pS* and *pR* forms can be prevented. For achieving the introduction of bulky groups after regulation of planar chirality, pillar[5]arene **H23** was designed with 2-(*S*)-methylbutoxy moieties on four benzene units and alkyl azide groups on the other benzene unit (Fig. 6b).[119] The dihaloalkane guest solvents regulated planar chirality as in the case of **H22**. Subsequent CuAAC click reactions to the two azide groups on **H23** with a bulky propargyl derivative resulted in planar chirality fixation. Surprisingly, diastereomerically pure **H23** in the *pR* form was obtained *via* crystallization with 1,2-dichloroethane. In subsequent CuAAC click reactions of the crystalline **H23**, an extremely high diastereomeric excess (≈95%) was achieved.

The planar chirality of **H22** and **H23** could be regulated using linear haloalkane solvents with high association constants with pillar[5]arene. By contrast, regulation of the planar chirality in *n*-alkane solvents with lower affinity with pillar[5]arene is challenging because they only have C–C and C–H groups. Our group also constructed a system in which planar chirality was regulated by achiral *n*-alkanes. Pillar[5]arene **H24** with stereogenic carbons and terminal bromine atoms on the rims showed adaptive planar chirality in response to the length of the *n*-alkane guests (Fig. 6c).[120] The steric bromo atoms played an important role in regulation of planar chirality. In short *n*-alkane solvents such as *n*-pentane, the *pS* form was favored because it placed the bulky bromo substituent inside the cavity, which resulted in a C–H/halogen interaction between **H24** and *n*-alkane guest solvents. On the other hand, in long *n*-alkane solvents such as *n*-heptane, the *pR* form, in which bulky bromo substituents were located outside the cavity, was favored because of steric hindrance. Notably, this planar chiral inversion between *pR* and *pS* forms could distinguish *n*-alkanes with chain lengths that differed by only one carbon atom.

Chiral inversion systems in response to achiral guest molecules could be also achieved based on pseudo[1]catenane of pillar[*n*]arenes. In 2013, we prepared the pseudo[1]catenane **H25** by CuAAC click reactions between 1,12-diazidododecane and dialkynylated pillar[5]arene. This was the first example of a chiral inversion system using pseudo[1]catenane (Fig. 7a).[121] Because the pillar[5]arene unit connecting the alkyl chain could rotate, inclusion and exclusion of the alkyl chain occurred. Thus, **H25** had four conformers: **in-*pS*-H25**, **in-*pR*-H25**, **out-*pS*-H25**, and **out-*pR*-H25**. Self-inclusion states of **H25** were more stable than de-threaded conformers. Thus, the conformers **in-*pS*-H25** and **in-*pR*-H25** could be obtained by chiral HPLC separation of a racemic mixture of **H25**. The obtained enantiomers showed chiral inversion upon addition of competitive achiral guests. The respective planar chiral inversions from **in-*pS*-H25** and **in-*pR*-H25** to **out-*pS*-H25** and **out-*pR*-H25** were monitored by CD signal changes. This chiral regulation was reversible, and the original CD intensity was restored on addition of competitive cyclic host molecules (*i.e.*, crown ether) because of extraction of guest molecules from the cavity.

The first pseudo[1]catenane-based chiral inversion system using pillar[6]arene was prepared by Yang and coworkers (Fig. 7b).[122] Pillar[6]arene-based pseudo[1]rotaxane **H26** bearing a ferrocene moiety was synthesized. As with **H25**, a racemic mixture of **H26** was separated into **in-*pS*-H26** and **in-*pR*-H26**, which confined the ferrocene moiety into the cavity. Chiral inversion was achieved by redox reactions of the ferrocene moiety because of the changing binding affinity with pillar[6]arene. On the basis of these reports, several pseudo[1]-rotaxane-based chiral inversion systems have been developed that respond to redox reactions,[123] photoirradiation,[124] metal ions,[125,126] temperature,[127] and pH.[128]

2.3 CPL signal responsive systems

The intrinsic planar chirality of pillar[*n*]arenes offers the potential for applications in CPL materials. However, most alkoxy-substituted pillar[*n*]arenes show emission only in the non-visible light region. Therefore, for CPL applications of the planar chirality of pillar[5]arenes, they must be designed to emit in the visible light region. Chen and coworkers first reported the pillar[5]arene-based CPL materials,[129] which triggered the exploration of various types of pillar[5]arene-based CPL materials.[107,130–136] These materials are usually prepared by introducing bulky conjugated moieties to simultaneously fix the planar chirality and provide luminescence in the visible light region. However, host–guest complexation does not produce a dramatic CPL response because the fixed planar chiral pillar[*n*]arenes do not exhibit large conformational changes in response to guest addition. To obtain a dramatic CPL response, Jiang and coworkers introduced luminescent moieties without

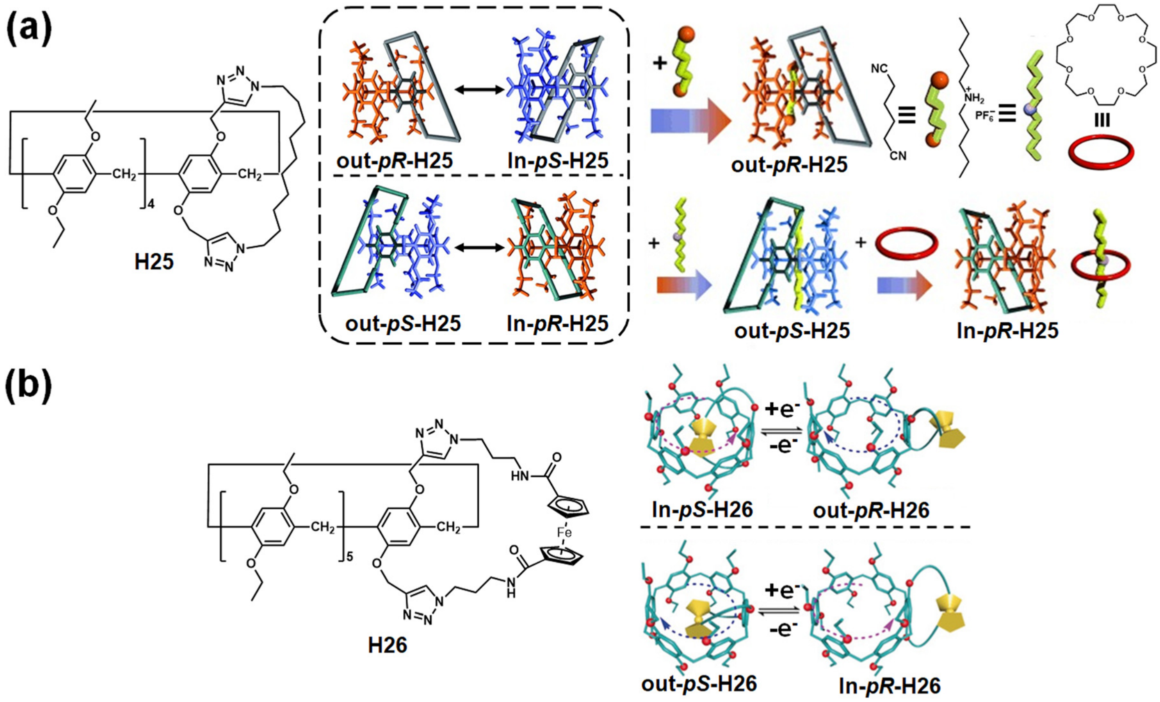

Fig. 7 Planar chiral inversion based on pseudo[1]catenane of (a) pillar[5]arene and (b) pillar[6]arene. Reproduced with permission from ref. 121 and 122 (Copyright 2013 and 2020 Wiley-VCH Verlag GmbH & Co. KGaA).

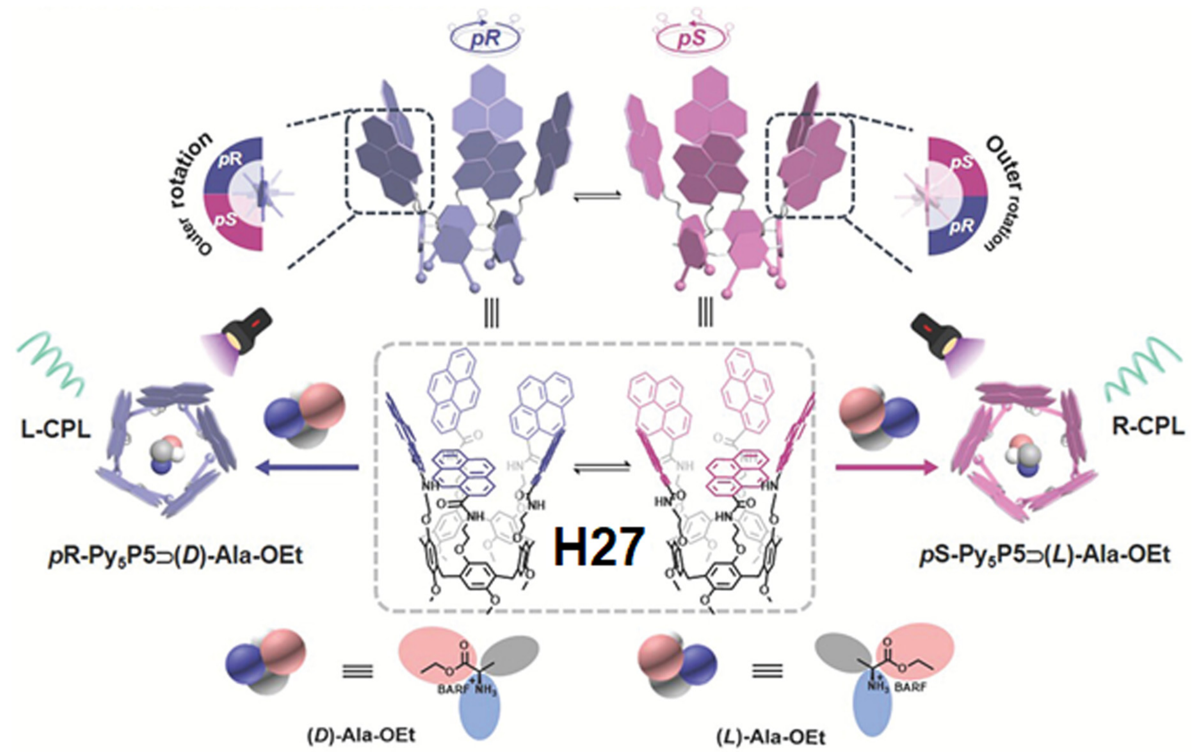

Fig. 8 Schematic representation of the switching of left- and right-handed CPL by addition of chiral guests. Reproduced with permission from ref. 137 (Copyright 2023 Wiley-VCH Verlag GmbH & Co. KGaA).

inhibition of planar chiral inversion (Fig. 8).[137] A rim-differentiated pillar[5]arene **H27**, in which all five pyrene units were located on one rim and all five methoxy groups were located on the other rim, was prepared. The methoxy groups were small enough to pass into the cavity of the pillar[5]arene and caused exchange between the *pS* and *pR* forms by inducing local rotation within 180°.[74] Therefore, chiral regulation was achieved by interaction with chiral guests (*i.e.*, L-/D-amino acid derivatives). Regulated planar chirality of the pillar[5]arene skeleton transferred into pyrene excimers, resulting in left- and right-handed CPL emission switching *via* chiral guest interactions with **H27**. The dissymmetry factor of luminescence $|g_{\mathrm{abs}}|$ reached 1.28×10^{-2}, and was comparable to those of fixed planar chiral pillar[5]arene based-CPL materials.[97,119,124]

3. Optically responsive systems *via* host–guest interactions in solid state

Host–guest complexation in the solid state of pillar[*n*]arenes has attracted attention since a 2015 report by our group.[55] Unlike in solution systems, efficient uptake of guest molecules is observed in solid-state systems because there is no competitive interaction with solvent molecules (Fig. 1d). The most important finding in solid-state complexation is that the crystal structure of the pillar[*n*]arene changes simultaneously with the uptake of guest molecules.[58,59] Pillar[*n*]arene crystals are "soft crystals" that change their structure in response to guest molecules such as alkane vapor molecules with low association constants. However, because alkoxy-substituted pillar[*n*]arenes are basically colorless and show no luminescence, additional substituent introduction into the pillar[*n*]arene skeleton or another strategy is necessary for the construction of optically responsive systems. In this section, we mainly introduce stimuli-responsive materials showing macroscopic changes, such as color and fluorescence changes, in response to microscopic events of the host–guest complexation.

3.1 Color responsive systems

In 2015, we demonstrated that perethylated pillar[5]arene **H11** crystals took up *n*-alkane vapor as a guest.[55] During this process, the crystal structure of **H11** was transformed. Because many reported chromic materials exhibit color changes induced by changes in crystal structure,[138] pillar[5]arene crystals have the potential to exhibit color changes with vapor uptake.[139,140] However, pillar[5]arene crystals are colorless, which suggests that the pillar[5]arenes need to be modified to color them before they can produce color changes with transformation of the crystal structure on vapor uptake. In 2017, we reported the first example of chromic materials with the pillar[5]arene skeleton. To color the pillar[5]arene, **H28** with one benzoquinone unit was prepared by oxidation of perethylated pillar[5]arene (Fig. 9a).[141] Crystalline **H28** was brown because of the formation of a CT complex between 1,4-diethoxybenzene and quinone units. When the crystals were exposed to *n*-hexane vapor, the crystals turned red. By contrast, no color change was observed when the crystals were exposed to

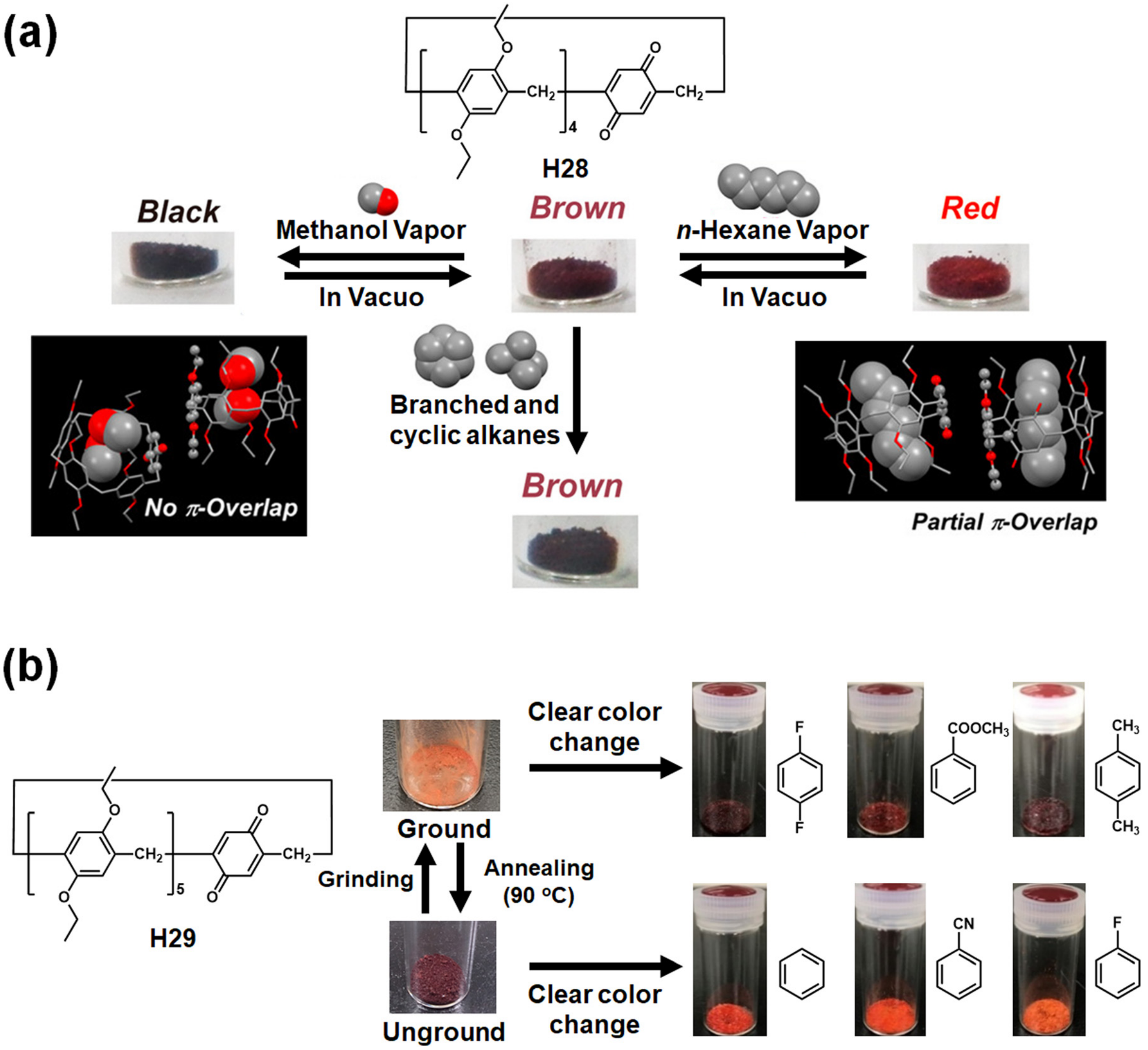

Fig. 9 (a) Schematic representation of the vapochromism of **H28**. Reproduced with permission from ref. 141 (Copyright 2017 American Chemical Society). (b) Schematic representation of the vapochromism and mechanochromism of **H29**. Reproduced with permission from ref. 142 (Copyright 2020 Royal Society of Chemistry).

2,2-dimethylbutane or 2,3-dimethylbutane with branched structures or cyclohexane with a cyclic structure. This was because linear *n*-hexane was suitable for the cavity size of pillar[5]arene but the other molecules were not. The crystals also turned black on exposure to methanol vapor. These color changes originated from changes in the crystal structure induced by the vapor uptake. Partial π-stacking between 1,4-diethoxybenzene and quinone units was observed in the X-ray crystal structure of the *n*-hexane complex. By contrast, no π-stacking was observed between 1,4-diethoxybenzene and quinone units in the methanol complex, which resulted in a difference in the crystal color. **H28** responded only to the vapors of linear molecules because the cavity size of the pillar[5]arene matched the sizes of these molecules. Solids prepared from pillar[6]arene are thus expected to respond to and show color changes with the vapors of bulky molecules, such as aromatic compounds, because the pillar[6]arene cavity accommodates bulky molecules. Pillar[6]arene **H29** containing one quinone unit was prepared by the same groups (Fig. 9b).[142] As expected, the solid **H29** showed color changes on uptake of aromatic vapor molecules. Surprisingly, solid **H29** showed color changes with both vapor (vapochromism) and grinding (mechanochromism). Grinding caused a color change in **H29** from dark red to light orange. Furthermore, this color change was reversible upon heating. Therefore, the color of the solid before vapor adsorption could be controlled by grinding. Unground solid **H29** was dark red and showed an obvious color change to light orange on exposure to benzene, cyanobenzene, and fluorobenzene vapors exposure. Ground solid **H29** was light orange and did not show an obvious color change on exposure to these vapors. On exposure to *p*-difluorobenzene, methyl benzoate, and *p*-xylene vapors, ground solid **H29** showed an obvious color change from light orange to dark red. By contrast, unground solid **H29**, which was already dark red, did not show an obvious color change with these vapors. Therefore, this work provide a new vapochromic system that can visually check the uptake of various aromatic vapors by adjusting the color of the starting state using mechanochromism.

The creation of CT complex crystals composed of a single molecule requires synthesis of donor and acceptor moieties within a single molecule. Thus, complicated molecular design is required. By contrast, preparation of CT complexes by co-crystallization of donor and acceptor molecules does not require additional modification. In 2020, Li and coworkers created CT complex crystals in tetrahydrofuran using the exo-wall interactions of perethylated pillar[5]arene **H11** with *N*,*N*′-bis(*n*-butyl)pyromellitic diimide (**PDI**) (Fig. 10a).[143] The obtained complex crystals were red because of CT interactions between **H11** and **PDI** but turned white when completely dried and the tetrahydrofuran in the complex crystals was removed. This color change indicated that the intermolecular CT interactions were disrupted. The activated complex crystals showed selective vapochromic responses to haloalkane vapors and exhibited drastic color changes from white to red or orange. No color change was observed upon exposure to vapors of other common organic compounds, such as methanol, ethanol, acetone, *n*-hexane, cyclohexane, benzene, toluene, *o*-xylene, ethylbenzene, and phenol. These vapochromic responses were attributed to the crystal structural transformation resulting in the formation of CT complexes between **H11** and **PDI**. The C–H/O and C–H/X hydrogen bonds between haloalkanes and **PDIs** in particular play an important role in the transformation to CT co-crystals and haloalkane-specific vapochromism.

This co-crystallization method is versatile. Vapochromism of co-crystals prepared using 1,2,4,5-tetracyanobenzene (**TCNB**) as the acceptor molecule was reported by Huang, Zhou, and coworkers (Fig. 10b).[144] With CH_2Cl_2 as the solvent, which could be encapsulated in the pillar[5]arene cavity, co-crystals between **H11** and **TCNB** were obtained with exo-wall CT interactions. After removal of CH_2Cl_2, activated complex crystals with brown color were obtained. This crystalline complex showed a distinct color change from brown to reddish brown or black upon adsorption of CH_2Cl_2 or aldehydes, respectively. The changes in color were attributed to rearrangement of CT interactions between **H11** and **TCNB** induced by the vapor uptake.

3.2 Fluorescence responsive systems

Pillar[*n*]arene crystals can adsorb vapors, which are triggered to induce changes in their crystal structures.[58,59] Therefore, they are promising molecular skeletons for the development of materials that exhibit vapor responsive emission changes. Our group found that all-ethyl-substituted pillar[6]arene **H30** crystals did not emit light in the visible region, but on adsorption of aromatic vapors, the crystals exhibited turn-on visible luminescence (Fig. 11).[145] This turn-on luminescence was selectively observed with vapors of different molecules. No visible luminescence was observed after exposure to toluene, *p*-xylene, aniline, *p*-difluorobenzene, and styrene vapors, but blue luminescence was observed after exposure to benzonitrile, methyl benzoate, and divinylbenzene (*para*- and *meta*-mixture) vapors. DFT and time-dependent DFT of the obtained single crystal structures revealed that the complexes of benzonitrile, methyl benzoate, and divinylbenzene produced luminescence through CT complexation.

While pillar[6]arenes with large cavities can take up aromatic vapors and result in CT complexation between the host and guest molecules, pillar[5]arenes cannot use this CT complexation strategy because of their smaller cavities, which cannot take up aromatic molecules. One way to solve this problem is to use pillar[5]arenes with luminescence. Yang and coworker prepared pillar[5]arene **H31** containing an acceptor dicyanobenzene moiety (Fig. 12a).[146] According to DFT and time-dependent DFT, the lowest unoccupied molecular orbital

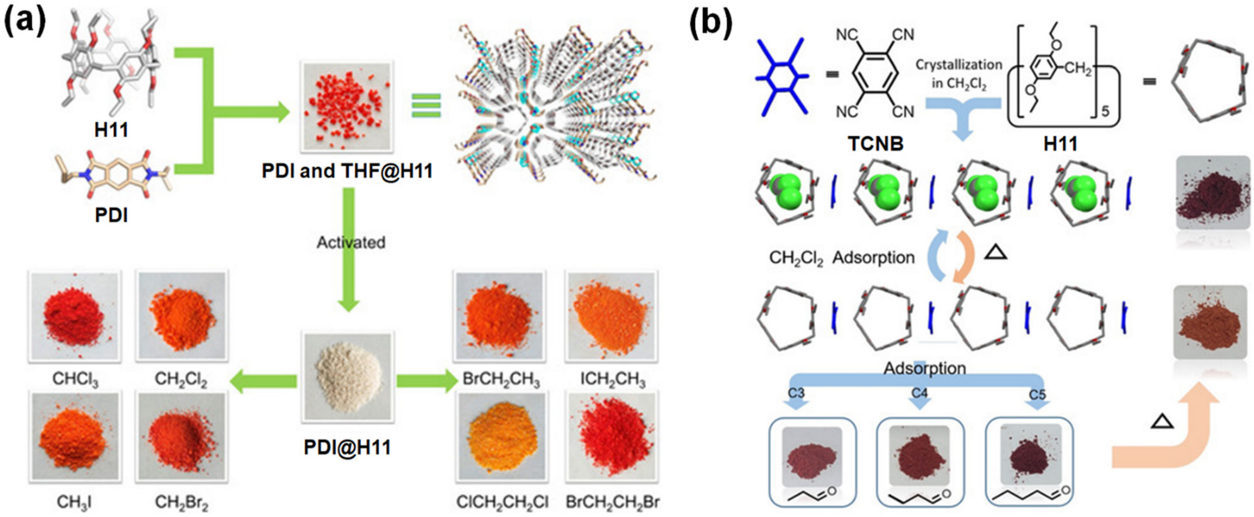

Fig. 10 (a) Schematic representation of the vapochromism of cocrystals between **H11** and **PDI** in response to haloalkane vapors. Reproduced with permission from ref. 143 (Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA). (b) Schematic representation of the vapochromism of cocrystals between **H11** and **TCNB** in response to alkyl aldehyde vapor. Reproduced with permission from ref. 144 (Copyright 2021 Wiley-VCH Verlag GmbH & Co. KGaA).

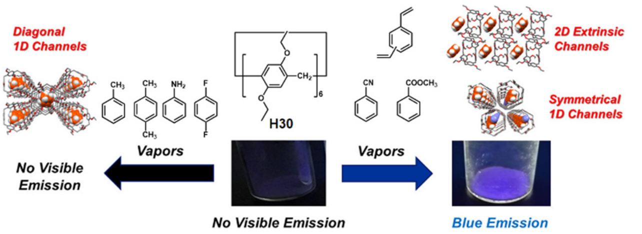

Fig. 11 Schematic representation of the turn-on vapoluminescence of **H30** in response to aromatic vapors. Reproduced with permission from ref. 145 (Copyright 2020 American Chemical Society).

(LUMO) was located on *p*-dicyanobenzene and the highest occupied molecular orbital (HOMO) was located on the dimethoxybenzene units. This resulted in emission derived from intramolecular TSCT. Although **H31** showed blue luminescence in the solid state, the color of the powder changed to yellow-green after absorption of acetonitrile, butyronitrile, valeronitrile, and isovaleronitrile vapors. By contrast, no luminescence change was observed for isobutyronitrile vapor because complexation did not occur with bulky isobutyronitrile. Furthermore, the color could be reversibly changed by vacuum drying and re-exposure to these vapors.

Huang, Zhu, and coworkers synthesized the fluorescent pillar[5]arene **H32** by introducing conjugated anthracene moieties *via* Sonogashira coupling reactions (Fig. 12b).[147] The desolvated **H32** crystals showed yellow luminescence derived from anthracene moieties. Exposure of the **H32** crystals to linear alkyl ketone vapors caused a change in the color of fluorescence. Interestingly, this fluorescence color change depended on the alkyl chain length of the linear alkyl ketones. A drastic fluorescence color change from yellow to green was observed upon exposure to the vapor of linear alkyl ketones containing 4–6 carbon atoms. By contrast, no clear color change was observed after exposure to linear alkyl ketones containing 7 or 8 carbon atoms. This selective color change could be explained by packing modes of anthracene units after the vapor uptake. According to the X-ray crystal structure analysis, after exposure to vapors of linear alkyl ketones containing 3, 7 or 8 carbon atoms, the **H32** crystals showed H-aggregation between anthracene units. Consequently, the crystals exhibited yellow excimer emission. On the other hand, **H32** crystals exposed to vapors of linear alkyl ketones with 4–6 carbon atoms showed green monomer emission because of J-aggregation between anthracene units. Overall, the introduction of fluorescent groups into the pillar[5]arenes allowed for preparation of a fluorescence responsive system on vapor exposure.

Huang, Jie, and coworker developed a new fluorescence color change system using the reaction of pillar[5]arene crystals

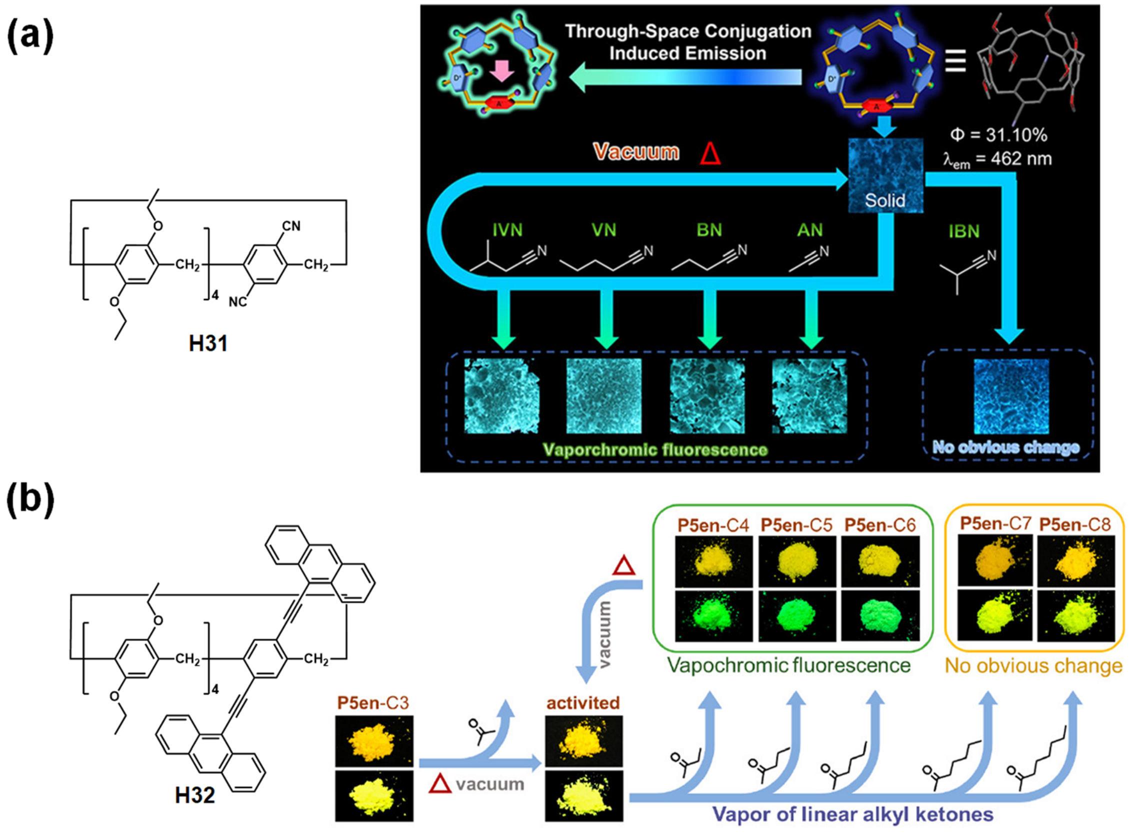

Fig. 12 (a) Schematic representation of the vapoluminescence of **H31** in response to common nitrile vapors. Reproduced with permission from ref. 146 (Copyright 2022 American Chemical Society). (b) Schematic representation of the vapoluminescence of **H32** in response to ketone vapors. Reproduced with permission from ref. 147 (Copyright 2019 American Chemical Society).

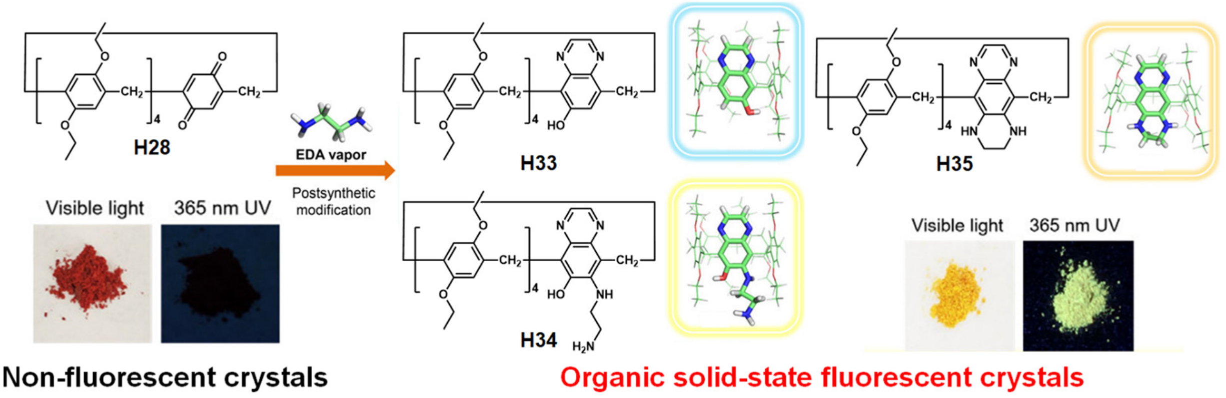

Fig. 13 Schematic representation of the solid–vapor post-synthetic modification of **H28** resulting in turn on vapoluminescence. Reproduced with permission from ref. 148 (Copyright 2020 American Chemical Society).

with vapor molecules (Fig. 13).[148] This system operates differently from the previously discussed crystal structure change with vapor uptake. The crystals of pillar[5]arenes containing one benzoquinone unit (**H28**) were dried and the activated crystals were brown and not emissive. After exposure to ethylenediamine, the color of the crystals gradually changed from dark-red to yellow. Moreover, the obtained yellow crystals exhibited yellow-green fluorescence under 365 nm UV light. This turn-on emission was caused by conversion of benzoquinone moieties of **H28** to conjugated planar quinoxaline units by Michael addition and subsequent condensation and dehydration. This converted **H28** to **H33**, **H34**, and **H35**, all of which contained a quinoxaline skeleton and showed fluorescence in the crystalline state. This turn-on vapoluminescence could be applied for sensing of ethylenediamine vapor. When **H28** crystals were exposed to linear alkylamines such as *n*-propylamine and *n*-butylamine, and linear alkyldiamines such as ethylenediamine, 1,3-diaminopropane, and 1,4-diaminobutane, only ethylenediamine vapor induced yellow-green fluorescence. This was because the other linear alkylamines and alkyldiamines did not form the quinoxaline structures.

4. Summary and outlook

We have summarized recent progress of optically responsive systems using pillar[*n*]arenes and host–guest interactions. Pillar[*n*]arenes have versatile functionality, which allows for easy installation of optically responsive groups. Moreover, the unique host–guest properties of pillar[*n*]arenes can generate selective responses. In particular, pillar[5]arenes can take up linear guest molecules, while pillar[6]arenes can take up bulky branched or cyclic guest molecules. The selective uptake of guest molecules induces color, fluorescence, CD, and CPL signal responses. In solution state, these optical responses are caused by changes in the structure of the pillar[*n*]arenes skeleton or by specific interactions between installed substituents and guest molecules (*i.e.*, PET and ET). The CD and CPL signals are caused by interconversion between *pS* and *pR* forms because of unit rotations. In this review, to achieve planar chiral regulation, we introduced three strategies: (i) diastereomeric host–guest complexation by adding chiral guest molecules to a racemic mixture of pillar[*n*]arene, (ii) formation of diastereomeric pillar[*n*]arenes by introducing chiral side chains into pillar[*n*]arene scaffolds, and (iii) chiral inversion systems based on pseudo[1]catenanes of pillar[*n*]arenes that respond to achiral guest molecules. In the solid state, the optical responses are mainly caused by changes in the crystal structure induced by guest molecule uptake. Microscopic events of host–guest complexation lead to changes in hierarchical assemblies and results in macroscopic changes, such as in color and fluorescence.

Despite numerous detailed studies on pillar[*n*]arene-based optically responsive systems, several challenges remain. These include (i) improving the sensitivity for practical utilization, (ii) achieving high dissymmetry factors by planar chiral regulation, (iii) expanding the current small variety of chiral guests for CD and CPL signal induction, and (iv) overcoming difficulties with crystal engineering, such as the design and prediction of crystal structures before and after guest molecule uptake. Future research could uncover many exciting potential uses of pillar[5]arene-based optically responsive systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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