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Stimuli-responsive blue fluorescent supramolecular polymers based on a pillar[5]arene tetramer†

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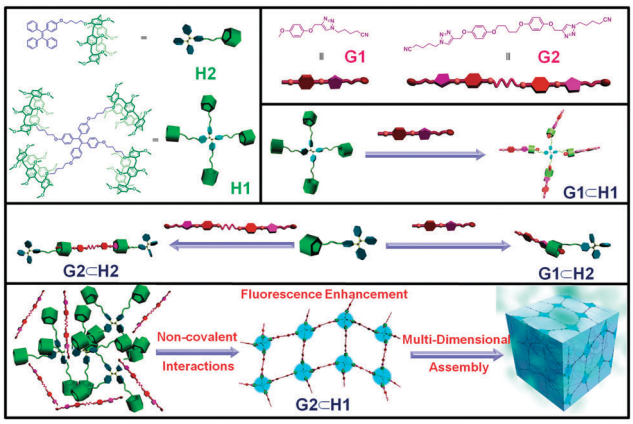
A tetraphenylethene-bridged pillarene tetramer with aggregation-induced emission properties forms an A_4/B_2-type supramolecular polymer and a gel with a symmetric neutral guest linker, showing a remarkable fluorescence emission enhancement in solution and the solid state and a good responsiveness to temperature and solvent composition.

Supramolecular polymerization and depolymerisation play a crucial role in biosystems, where relatively simple molecular precursors are brought together or separated in a precisely specific manner through non-covalent interactions with the stimulation of the environment.[1] Inspired by the captivating process of self-assembly in biosystems, considerable effort has been devoted to the design of artificial functional supramolecular systems.[2,3] Pillarenes (or pillar[*n*]arenes),[4] as a new generation of supramolecular macrocyclic receptors, firstly reported in 2008,[4a] consisting of hydroquinone units linked by methylene bridges at 2,5-positions, have been the focus of much research and have shown great potential in molecular switches/machines,[5] artificial transmembrane channels,[6] metal–organic frameworks,[7] controlled drug delivery systems,[5a,b,8] sensors,[9] supramolecular polymers,[3d,10] hybrid absorbents,[11] virus inhibitors,[12] *etc.*, owing to their unique structures and superior host–guest properties.[13,14] Compared with other major synthetic macrocycles, pillarene derivatives have recently shown excellent binding abilities towards neutral guest molecules[14] in organic solvents, facilitating a new pathway for supramolecular self-assembly of neutral host–guest species in organic media with special physical, chemical and optical properties.

Significantly, bridged pillarenes, such as dimers[10a,b] and trimers,[10c] have been reported to form linear and multi-dimensional assemblies upon binding with guest linkers, *e.g.*, viologens. However, pillarene tetramers or pentamers have not yet been synthesized, especially incorporating fluorogenic functionalities, which is hoped to provide a versatile platform for the construction of stimuli-responsive supramolecular polymers/gels with specific properties for various applications in sensors, photonics, electronics, biomedicine, *etc.*



Scheme 1 Schematic illustration of the construction of fluorescent supramolecular polymers of **G2⊂H1** and other host–guest complexes of **G2⊂H2**, **G1⊂H1** and **G1⊂H2** for comparison.

Herein, we report the synthesis of the first tetrameric pillarene, *i.e.*, tetraphenylethene (TPE)-bridged pillar[5]arene (P5) tetramer, TPE-$(P5)_4$ (**H1**), and its interaction with a newly designed triazole-based neutral linker (**G2**) to construct pillarene-based stimuli-responsive supramolecular gels with strong blue fluorescence (Scheme 1) for the first time. Considering the significance of supramolecular polymerization and depolymerization in nature,[1] the on–off switchable fluorescent properties of **G2⊂H1** based on supramolecular assembly–disassembly *via* the aggregation-induced emission (AIE) mechanism may facilitate the evolution of novel fluorescent probe technology for the labeling and tracking of cells, proteins and nucleic acids.

The compounds, *i.e.*, **H1**, TPE-P5 monomer (**H2**) and TPE-$(monomer)_4$ (**H3**), were synthesized according to the synthetic routes provided in the ESI.† Briefly, tetrahydroxyl TPE was synthesized by Cross McMurry reactions[15] between two bis(4-hydroxyphenyl)-methanones. Then **H1** was synthesized by introducing four bromobutyl mono-substituted P5 units (CoP5s) to react with the four hydroxy groups of the tetrahydroxyl TPE, catalyzed by K_2CO_3 and

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KI in MeCN. Monohydroxyl TPE was synthesized by Cross McMurry reactions of (4-hydroxyphenyl) phenyl methanone and benzophenone, and then further reacted with CoP5 in MeCN to give **H2** (Fig. S5–S12, ESI†). Meanwhile, the monomer of CoP5, *i.e.*, 1-(4-bromobutoxy)-4-methoxy benzene, was also reacted with tetrahydroxyl TPE to give **H3** without a host cavity as a control compound. All the new compounds were fully characterized by ^{1}H NMR, ^{13}C NMR and MALDI-TOF MS spectroscopy (Fig. S4–S12, ESI†). **H1** and **H2** were endowed with AIE characteristics in the mixed solvents of H_2O–THF, indicating similar fluorescent behavior to traditional TPE derivatives and providing diverse functionalities with potential applications (Fig. S22, ESI†).

On the other hand, we designed and synthesized an asymmetric neutral guest **G1** by the Cu^{I}-catalyzed Huisgen alkyne–azide 1,3-dipolar cycloaddition, the so-called CuAAC 'click' reaction (Fig. S14–S16, ESI†).[16] Before we set out to study the supramolecular self-assembly properties of the above host–guest compounds, the inclusion complexation of the neutral guest monomer (**G1**) and the model host compound (**H2**), with only one pillarene cavity as the recognition motif, has been investigated by isothermal titration calorimetry (ITC), which is a powerful method for measuring the host–guest association constants (K_a) and thermodynamic parameters (Fig. S26–S27, ESI†). Chloroform was chosen as the solvent for investigating the interactions between **G1** and **H2**. The titration data can be well fitted by computer simulation using the "one set of binding sites" model, further confirming the stoichiometry of the complexation between **G1** and **H2** to be 1 : 1. The K_a value was determined to be $(1.46 \pm 0.05) \times 10^4$ M^{-1}, indicating a strong binding between the pillarene cavity and the neutral guest moiety. The inclusion complexation of **G1** and **H2** is primarily driven by favorable enthalpy changes ($\Delta H^\circ = -57.76 \pm 4.19$ kJ mol^{-1}), accompanied by negative entropic changes ($T\Delta S^\circ = -34.07 \pm 0.12$ kJ mol^{-1}), which manifests that the binding process is mainly caused by C–H$\cdots\pi$ interactions, C–H$\cdots$N/C–H$\cdots$O hydrogen bonds and van der Waals forces.[4b]

Fabrication of highly efficient luminescent supramolecular polymers based on pillarenes is in urgent need for the construction of stimuli-responsive soft matter with unique optical and sensing properties. Chloroform, as an extremely favorable solvent for **H1** and **G2**, was chosen as a solvent medium for the study of **H1–G2** assembly. The pillarene tetramer (**H1**) with four recognition sites connecting through one TPE core can include the linear neutral guest dimer (**G2**) (Fig. S13–S21, ESI†) consisting of two triazole units. **H1** dissolved in $CHCl_3$ shows relatively weak fluorescence; however, upon gradual addition of **G2**, the PL intensity (Fig. 1a, b and e) of the mixture is continuously enhanced. This phenomenon can be explained by the mechanism of AIE proposed by Tang *et al.*,[17] attributing to the TPE core of **H1**: (a) when **G2** is added to **H1** solution, supramolecular assembly occurs due to the efficient inclusion complexation of **H1** and ditopic guest **G2**; (b) **H1** molecules are linked together by this highly efficient host–guest binding where the TPE cores of **H1** molecules are maximally brought close to each other; (c) therefore, the internal rotations of the molecules have been largely restricted, thus blocking the nonradiative relaxation channel and populating the radioactive decay to the ground state,[17] making the material emissive.

To further confirm the explanation that fluorescence enhancement results from the supramolecular assembly of **H1** and **G2**, control experiments have been performed. When **G2** is added to

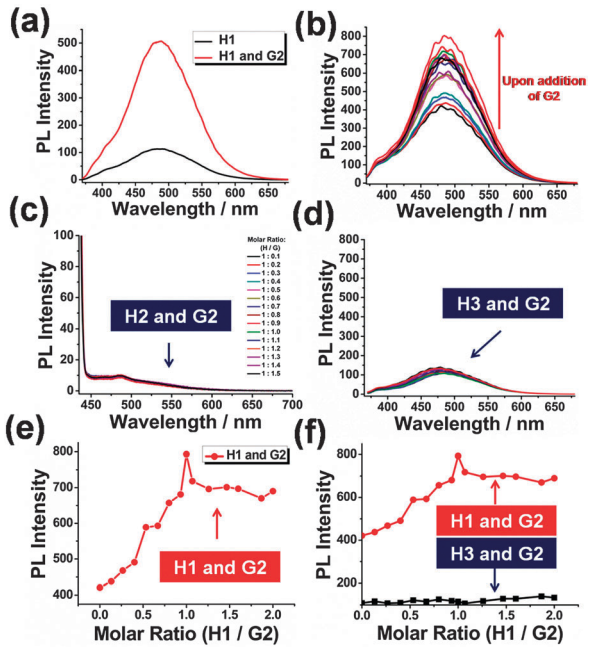

Fig. 1 Fluorescence emission spectra of (a) **H1** (black line) and **G2**⊂**H1** (red line) (λ_{ex} = 350 nm; λ_{em} = 481 nm; slit widths: ex. 5 nm, em. 5 nm; 25 °C, concentration: [**H1**] = 100 μM, [**G2**] = 400 μM); (b) **G2**⊂**H1** (λ_{ex} = 350 nm; λ_{em} = 481 nm; slit widths: ex. 5 nm, em. 5 nm; 25 °C, concentration: [**H1**] = 200 μM, [**G2**] = 0 μM, 53 μM, 106 μM, 159 μM, 212 μM, 260 μM, 318 μM, 373 μM, 400 μM, 426 μM, 506 μM, 586 μM, 640 μM, 693 μM, 746 μM, 800 μM); (c) **G2**⊂**H2** (λ_{ex} = 425 nm; slit widths: ex. 10 nm, em. 10 nm; 25 °C, concentration: [**H2**] = 1 μM, [**G2**] = 0.0 μM, 0.2 μM, 0.3 μM, 0.4 μM, 0.5 μM, 0.6 μM, 0.7 μM, 0.8 μM, 0.9 μM, 1.0 μM, 1.1 μM, 1.2 μM, 1.3 μM, 1.5 μM, 1.7 μM, 2.0 μM; [**H2**] = 0 μM, [**G2**] = 2.0 μM); (d) **G2**⊂**H3** (λ_{ex} = 350 nm; λ_{em} = 489 nm; slit widths: ex. 5 nm, em. 5 nm; 25 °C, concentration: [**H3**] = 200 μM, [**G2**] = 53 μM, 106 μM, 159 μM, 212 μM, 260 μM, 318 μM, 373 μM, 400 μM, 426 μM, 506 μM, 586 μM, 640 μM, 693 μM, 746 μM, 800 μM); (e) fluorescence emission intensity changes of **G2**⊂**H1** at λ_{em} = 481 nm; (f) the comparison of fluorescence emission intensity changes of **G2**⊂**H1** (at λ_{em} = 481 nm, red line) and **G2**⊂**H3** (at λ_{em} = 481 nm, black line).

the $CHCl_3$ solution of **H2** (Fig. 1c), which possesses only one pillarene and can only form 1 : 2 host–guest complexes with **G2** instead of forming a supramolecular network, there is no obvious fluorescence enhancement. The 1 : 2 inclusion complex, *i.e.*, **G2**⊂(**H2**)$_2$, is dissolved well in $CHCl_3$ without any internal rotations restricted. Moreover, **H3**, *i.e.*, TPE functionalized with four monomers of P5, was also synthesized as a control compound to **H1**. The mixture of **H3** and **G2** shows no fluorescence enhancement with the continuous addition of **G2** (Fig. 1d and f) because they are dispersed in $CHCl_3$ individually without any host–guest complexation due to the lack of host cavities. All the above experiments indicated that supramolecular self-assembly occurs between **H1** and **G2** in $CHCl_3$ and there was an obvious fluorescence enhancement accompanied with their supramolecular polymerization attributing to the restriction of internal rotation (RIR) of the TPE cores of **H1**. The high-order complexes *via* supramolecular interactions provide us innovative thoughts to simulate the process in biosystems accompanied with fluorescence for sensing and tracking.

Compared with traditional polymers, one of the important features of supramolecular polymers is the ease of controlling

its assembly–disassembly by adjusting those non-covalent interactions between the building blocks, mimicking the polymerization and depolymerization in biological systems. Supramolecular polymers responsive to solvent composition are degradable new materials upon changing the polarity of the mixed solvent.[3d] Herein, we found that solvent composition also plays a key role in influencing the fluorescence behavior of **G2⊂H1**. We tested several mixed solvents to show the influence of solvent composition on the assemblies by studying the intensity changes of their fluorescent emissions. According to the previous experiments, **H1** and **G2** can form stable supramolecular polymers in pure $CHCl_3$ owing to their strong binding affinity. Therefore, we use $CHCl_3$ as the basic solvent to prepare **G2⊂H1** solutions where the concentration of **H1** and **G2** is 10 μM and 20 μM, respectively. As shown in Fig. S29 (ESI†), when **G2⊂H1** was prepared in a mixed solvent of CH_3CH_2OH : $CHCl_3$ (v/v = 1 : 1), its PL intensity was enhanced. This is because **H1** and **G2** cannot be dissolved in pure CH_3CH_2OH and the intramolecular rotations of TPE cores of **H1** are further inhibited as the viscosity of the mixture is increased. When other mixed solvent systems, *i.e.*, CH_2Cl_2 : $CHCl_3$ (v/v = 1 : 1), CH_3COCH_3 : $CHCl_3$ (v/v = 1 : 1), and CH_3CN : $CHCl_3$ (v/v = 1 : 1), were employed, the PL intensity exhibited a small (24.1%, I_0 = PL intensity of **G2⊂H1** in pure $CHCl_3$) or remarkable decrease (52.5% and 49.3%), in a sharp contrast to the CH_3CH_2OH : $CHCl_3$ (v/v = 1 : 1) situation. These phenomena can be ascribed to the fact that in pure $CHCl_3$, the molecular recognition events between pillarene moieties of **H1** and guest **G2** are more favored compared with those in the other three mixed solvents.

In the process of molecular recognition and supramolecular self-assembly, elevated temperatures always decrease the stabilities of host–guest systems due to the accompanying more unfavorable entropy term ($T\Delta S^\circ$) governing their complexation free energies.[2b,18] We envisage that the increase of system temperature will result in the decrease of the PL intensity since elevated temperature will weaken the binding affinities between pillarene hosts and neutral linear guests. The experimental results showed that upon gradually increasing the solution temperature from 0 °C to 57 °C (b.p. of $CHCl_3$ is 61.2 °C), the fluorescent emission intensity of the $CHCl_3$ solution of **H1** (0.1 mM) and **G2** (0.2 mM) decreased by 53.3% (calculated through the measurement of the FL intensity at 488 nm) (Fig. 2a and c). In contrast, the fluorescent emission intensity of the mixture of **H1** and **G2** increased by 110.7% (calculated through the measurement of the FL intensity at 488 nm) (Fig. 2b and d) upon lowering the temperature from 57 °C to 0 °C. All the above experiments indicated that the temperature-dependent fluorescent change is reversible, which can be repeated for many cycles. These experimental data proved that the stability of the formed supramolecular assemblies of **H1** and **G2** in $CHCl_3$ governs the fluorescent emission intensity by affecting the degree of the RIR of TPE cores in **H1**.

Intriguingly, the inclusion complexation of **H1**, with four **P5** macrocycles, and **G2**, as a ditopic linear linker, in $CHCl_3$ induced gelation successfully at a concentration of 70 mM (C_{H1} = 70 mM, C_{G2} = 140 mM, molar ratio: **H1** : **G2** = 1 : 2) due to the formation of A_4/B_2-type supramolecular polymers to result in a large-scale multiple complexes. This solution-gelation process has been shown in Fig. 3e, where the solution stops flowing at high concentrations upon turning the test tube upside down. Controlled experiments

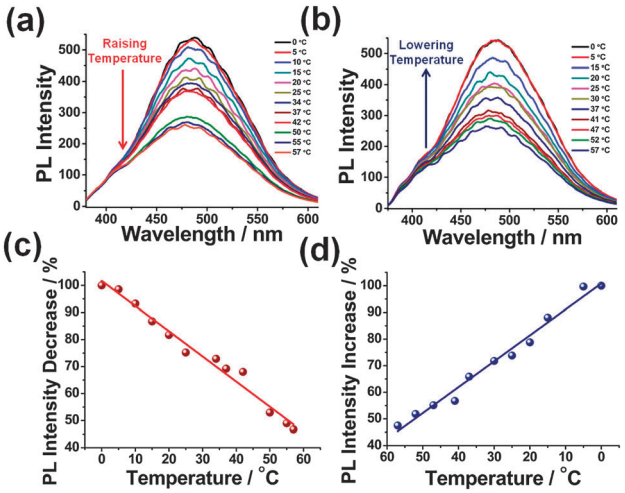

Fig. 2 Fluorescence emission spectra of **G2⊂H1** (a) upon elevating the temperature and (b) lowering the temperature. (λ_{ex} = 364 nm; λ_{em} = 488 nm; slit widths: ex. 5 nm, em. 5 nm; 25 °C, concentration: [**H1**] = 100 μM, [**G2**] = 200 μM); (c) relative emission intensity changes at λ_{em} = 488 nm when elevating the temperature from 0 °C to 57 °C (PL intensity decrease/% = $I/I_0 \times 100\%$); (d) relative emission intensity changes at λ_{em} = 488 nm when lowering the temperature (PL intensity increase/% = $I/I_0 \times 100\%$). I_0 represents the emission intensity at 0 °C.

show that, at the same concentrations and/or molar ratios of host and guest, none of the $CHCl_3$ solutions of the **H2–G2** complex, the mixture of **H3** and **G2**, and individual **H1** or **G2** forms gels, indicating that they could not form supramolecular networks for gelation and host–guest design is extremely important (Fig. 3a–d). Significantly, the gels constructed from **G2⊂H1** exhibited a strong blue fluorescence emission with the maximum wavelength of 492 nm as observed by solid-state fluorescence spectroscopy (Fig. 3g).

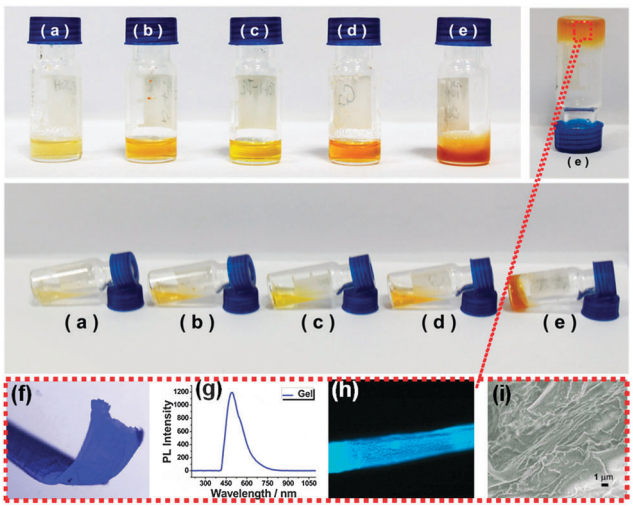

Fig. 3 Photographs of (a) **G2⊂H2**, (b) **G2⊂H3**, (c) **H1**, (d) **G2**, and (e) **G2⊂H1** (upright and upside down); (f) confocal laser scanning microscope image of the supramolecular gel constructed of **G2⊂H1** (λ_{ex} = 405 nm); (g) solid-state fluorescence emission spectra of the supramolecular gel constructed of **G2⊂H1** observed by fluorescence microscopy (λ_{em} = 488 nm); (h) fluorescent images observed by the fluorescence microscopy (λ_{ex} = 365 nm, at magnification ×200); (i) SEM images of the gel (scale bar: 1 μm).

Meanwhile, fluorescence microscopy (Fig. 3h) and confocal laser scanning microscopy (CLSM) (Fig. 3f) further revealed the gel morphology of **G2⊂H1** in a micrometer scale and its PL properties of strong blue emission. In addition, the scanning electron microscopy (SEM) image of the gel also shows its glutinous surface morphology (Fig. 3i).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. S30 and S31, ESI†) are used as special methods to characterize the thermal stabilities of the supramolecular gel. Especially, TGA data show that the gel has no obvious decomposition from 175 °C to 200 °C, nevertheless, from the DSC curve, there are three peaks at 177.1 °C, 182.2 °C, and 195.7 °C, ascribing to the physical transformation of supramolecular aggregation states of the gel instead of the self-decomposition of any components.

In summary, we report the design and synthesis of a new pillarene tetramer derivative (**H1**) with a TPE core and four pillarene cavities, which can bind strongly to the linear neutral guest linker **G2** with cyano sites and triazole sites to form A_4/B_2-type supramolecular polymers, **G2⊂H1**, in $CHCl_3$. Fascinatingly, the supramolecular self-assembly of **H1** and **G2** results in dramatic blue fluorescent emission enhancement due to the RIR of TPE cores. The fluorescent intensity of **G2⊂H1** assemblies in $CHCl_3$ showed good temperature and solvent responsiveness. Furthermore, blue supramolecular gels can be obtained at a host concentration of 70 mmol L^{-1} with a host–guest molar ratio of 1 : 2. To the best of our knowledge, this is the first report on pillarene derivatives with intriguing fluorescent enhancement phenomena, which paves a new way of efficient fabrication of pillarene-based fluorescent materials.

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