ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2014, 50, 9122

Received 28th April 2014,
Accepted 17th June 2014

DOI: 10.1039/c4cc03127j

www.rsc.org/chemcomm

Controllable aggregation-induced emission based on a tetraphenylethylene-functionalized pillar[5]arene *via* host–guest recognition†

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A novel TPE-functionalized pillar[5]arene (TPEP5) was successfully synthesized, and the motion of the TPE motif was restricted *via* pillararene-based host–guest recognition-mediated cross-linking, resulting in the efficient "turn-on" of fluorescence emission based on the AIE mechanism.

Molecules with aggregation-induced emission (AIE)[1] or aggregation-induced enhanced emission (AIEE)[2] characteristics have provided a promising platform for design and creation of efficient light emitters ranging from optical materials to sensors, owing to the enhanced emission in their aggregate or solid-state forms.[3] Since the first AIE molecule reported by Tang *et al.* in 2001,[1a] a wide variety of AIE molecules have been synthesized based on the mechanism of restriction of intramolecular motions (RIM).[1b,3b] Among various AIE molecules, tetraphenylethene (TPE) and its functionalized derivatives can be readily obtained *via* facile synthetic transformations, which are non-emissive in the molecularly dissolved state, but enhanced fluorescence emission could be achieved in both the aggregated form and the solid state.[4] In contrast to the aggregation-caused quenching (ACQ) effect of conventional organic luminophores, TPE-based AIE-active materials are demonstrated to have improved efficiency and sensitivity as chemosensors, bio-probes, and solid-state emitters and have already shown practical applications in these fields.[5] For example, Tang and co-workers synthesized a peptide-conjugated TPE derivative, which could be used as a live-cell-permeable, fluorescent light up probe for real-time cell apoptosis imaging.[6] In addition, Zhang *et al.* demonstrated that the TPE derivatives containing adenine or thymine moieties could be used as "turn on" chemosensors for selective detection of Ag^+ and Hg^{2+} ions.[5c]

Recently, non-covalent interactions such as host–guest recognition have been proved to be efficient strategies to restrict the intramolecular motions of TPE molecules, concomitantly accompanied by the turn-on of fluorescence emission *via* the AIE mechanism.[7] For example, Liu and co-workers integrated the concept of AIE with the specific host–guest supramolecular recognition between K^+ ions and crown ether moieties to develop effective fluorometric K^+ probes.[7a] Considering the unique structure and interesting host–guest chemistry of pillararenes, which can form supramolecular inclusion complexes with various kinds of linear guests,[8] the grafting of pillararenes onto the periphery of TPE can provide a novel strategy for fabricating various functional AIE luminogens and achieving the fluorescent detection of various types of guest compounds mediated by the pillararene-based host–guest interactions.[9] Herein, we designed and for the first time successfully synthesized a TPE-functionalized pillar[5]arene (**TPEP5**) by attaching four DMPillar[5]arene (**DMP5**) groups onto the periphery of TPE (Scheme 1). It was found that **TPEP5** dissolved in $CHCl_3$–acetone solution with negligible fluorescence emission, whereas, upon addition of the guest molecule (**G1**), **TPEP5** could be effectively induced to aggregate due to the pillararene-based host–guest recognition-mediated cross-linking *via* the formation of the **TPEP5**⊃**G1** (1 : 2 molar ratio) inclusion complex, which concomitantly resulted in the "turn-on" of fluorescence emission based on the AIE mechanism. Moreover, the fluorescence "turn-off" was observed upon the gradual addition of adiponitrile (**G3**, a competitive guest), which was easily visualized by the naked eye. Thus, this novel supramolecular system based on the **TPEP5**⊃**G1** complex creates unique possibilities to fabricate novel types of pillararene-based fluorescent probes.

The TPE-functionalized pillar[5]arene (**TPEP5**) was prepared by attaching four DMPillar[5]arene (**DMP5**) groups onto the periphery of TPE through the alkyne–azide click reaction (Scheme S1, ESI†).[10] To the best of our knowledge, this is the

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† Electronic supplementary information (ESI) available: Synthesis and characterization data; determination of the association constants; fluorescence spectra and DLS study. See DOI: 10.1039/c4cc03127j

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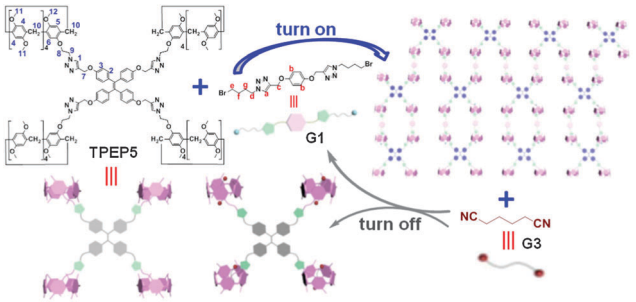

Scheme 1 Schematic illustration of the construction of the luminescent supramolecular aggregates based on aggregation-induced emission (AIE) of pillar[5]arene-functionalized tetraphenylethene (**TPEP5**), induced by host–guest recognition-mediated cross-linking between **G1** and pillar[5]arene moieties, and its application in the detection of adiponitrile.

first example of successful synthesis of a TPE-functionalized pillar[5]arene (**TPEP5**), which could be used to fabricate functional luminescent supramolecular aggregates induced by host–guest recognition-mediated cross-linking between **G1** and pillar[5]arene moieties based on the AIE mechanism.

The complexation between **TPEP5** and **G1** was initially investigated by ^{1}H NMR spectroscopy as shown in Fig. 1. The proton NMR spectra of **TPEP5**, **G1**, and a mixture of **TPEP5** and 4 equiv. of **G1** showed that this complexation system is a fast-exchanging process on the proton NMR time scale. As can be seen from Fig. 1b, after complexation the peaks of phenyl protons H_4, H_5, H_6, methylene and methoxyl protons H_{10}, H_{11}, H_{12} from the pillar[5]arene, and triazole protons H_1 on **TPEP5** shifted downfield slightly. The proton signals derived for H_d, H_e, H_f, H_g, and H_a of **G1** shifted upfield remarkably due to the shielding effect of the electron-rich cavities of the pillar[5]arene on **TPEP5**. While, no obvious change was observed for the protons H_b and H_c on **G1**. The above results revealed that the pillar[5]arene motifs on **TPEP5** were fully threaded by guest **G1** with the protons H_d, H_e, H_f, H_g and H_a in the pillar[5]arene cavities and other protons H_b and H_c out of the cavities. In addition, the ^{1}H NMR spectrum of a mixture of the model compound DMpillar[5]arene (**DMP5**) and 0.5 equiv. of **G1** was also investigated

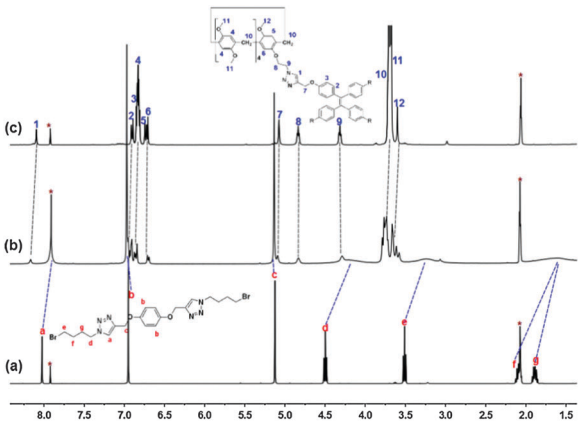

Fig. 1 ^{1}H NMR spectra ($CDCl_3$/acetone-d_6 (1 : 8, v/v), 300 MHz, 298 K) of (a) 5 mM **G1**; (b) 5 mM **TPEP5** and 20 mM **G1**; (c) 5 mM **TPEP5**.

and similar complexation-induced chemical shift changes were observed (Fig. S21, ESI†). Moreover, a 2D NOESY experiment was also performed to study the host–guest complexation between **DMP5** and **G1** (Fig. S23, ESI†). NOE correlation signals were observed between protons H_1 on **DMP5** and H_d, H_e, H_f, H_g on **G1**, as well as protons $H_{2'}/H_{3'}$ on **DMP5** and H_d, H_e, H_f, H_g on **G1**, which also confirmed the above threading binding mode.

Further investigation of the complex stoichiometry between **TPEP5** and **G1** was carried out by Job's plot method using model compound **DMP5**, and the result indicated that a 2 : 1 stoichiometry complex was formed between **DMP5** and **G1** (Fig. S22, ESI†), which further confirmed our envision that the guest molecule **G1** could serve as a cross-linker to bind with two molecules of **DMP5** motifs (Fig. S31, ESI†), leading to the aggregation of **TPEP5** and form a supramolecular network (for details, see ESI,† Fig. S34).[8d] In order to investigate the binding affinity of the pillar[5]arene–**G1** recognition motif, model compounds **DMP5** and **G2** (1-(4-bromobutyl)-4-((4-methoxyphenoxy)-methyl)-1*H*-1,2,3-triazole, analogues of **G1**) were applied for the ^{1}H NMR titration experiments, where the association constant (K_a) for the formation of the 1 : 1 **DMP5**⊃**G2** complex was calculated to be (7.30 ± 0.49) × 10^2 M^{-1} ($CDCl_3$–acetone-d_6, Fig. S26–S28, ESI†).

Considering the AIE feature of the TPE core in **TPEP5** and based on the above established novel **DMP5**⊃**G1** (2 : 1 molar ratio) supramolecular inclusion complex, we envisage that the addition of **G1** will induce the aggregation of **TPEP5**, which concomitantly results in the "turn-on" of fluorescence emission based on the AIE mechanism. Thus the fluorescence properties of such host–guest recognition-induced aggregation of **TPEP5** were further investigated. In preliminary experiments, we found that the choice of solvents also played important roles in observing the host–guest recognition-induced AIE. Lots of efforts were therefore made in the initial stage, searching for an appropriate solvent system, and finally, $CHCl_3$/acetone (1/8, v/v) was selected as the best solvent system for such supramolecular aggregation (for details, see Fig. S25, ESI†). It was found that **TPEP5** dissolved in $CHCl_3$/acetone (1/8, v/v) showed negligible fluorescence emission due to the efficient nonradiative annihilation caused by the intramolecular rotation of the phenyl rings in the TPE core of **TPEP5**[1a] (Fig. 2, inset A). However, when **G1** was added into the above **TPEP5** solution, the fluorescence emission increased gradually due to the formation of a supramolecular network and the rotation of phenyl rings in the TPE core of **TPEP5** is restricted. As shown in Fig. 2, a dramatic emission enhancement was observed when 16.0 equiv. of **G1** was added, and this fluorescence enhancement can be easily distinguished by the naked eye when illuminating the solution with UV light (365 nm) as indicated in the inset of Fig. 2, which further supports the proposed AIE mechanism. Moreover, the quantum yield of **TPEP5** with 8.0 equiv. of **G1** was determined to be 12.3%, measured by using quinine sulfate in 0.1 M H_2SO_4 (quantum yield = 54.6%) as the standard (Fig. S32, ESI†).

According to the previous report, dinitrile compounds show very strong binding affinities with the pillar[5]arene based on the cooperative multiple hydrogen bond and dipole–dipole interactions.[8f]

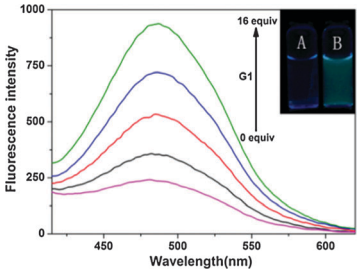

Fig. 2 Fluorescence spectral changes of **TPEP5** (0.04 mM) upon gradual addition of **G1** (0–0.64 mM) in $CHCl_3$/acetone (1/8, v/v) (λ_{ex} = 330 nm). The inset shows the photographs of the solution of **TPEP5** in the (A) absence and (B) presence of **G1** (0.64 mM) under UV light (365 nm) illumination at 298 K.

Hence, we envisioned that the complexation between **TPEP5** and **G1** could also be destroyed after the addition of size-fit dinitrile, such as adiponitrile, resulting in the fluorescence "turn-off" of the above supramolecular **TPEP5**⊃**G1** system. To investigate the fluorescence sensing effect of the above **TPEP5**⊃**G1** system for adiponitrile, fluorescence titration experiments were performed by adding different concentrations of adiponitrile (**G3**) to the **TPEP5**⊃**G1** system in $CHCl_3$/acetone (1/8, v/v). As shown in Fig. 3, significant quenching of the fluorescence intensity was observed upon the gradual addition of adiponitrile, which could also be easily visualized by the naked eye when illuminating the solution with UV light (365 nm). For the quenching of the fluorescence, a possible reason is that after addition of the completive guest **G3**, a more stable inclusion complex **TPEP5**⊃**G3** was formed (Fig. S29 and S30, ESI†), which could not lead to the cross-linking of **TPEP5** due to the fact that **G3** can bind with only one molecule of **DMP5**, generating a simple 1 : 1 inclusion complex. Therefore, **TPEP5** could not be induced to aggregate and result in the fluorescence "turn-off".

Furthermore, transmission electron microscopy (TEM) was also used to provide further insight into the size and shape of the supramolecular aggregates formed from **TPEP5** and **G1**. As shown in Fig. 4, spherical aggregates with a diameter of ~2 μm were observed for the supramolecular aggregates formed in $CHCl_3$–acetone solution (Fig. 4a and b). Moreover, the dynamic light scattering (DLS) measurements showed that different size distributions were observed and the mean size of the above

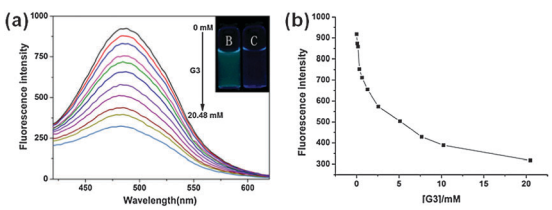

Fig. 3 (a) Fluorescence quenching of a solution of **TPEP5** (0.04 mM) and **G1** (0.64 mM) upon gradual addition of adiponitrile (**G3**, 0–20.48 mM), $CHCl_3$/acetone (1/8, v/v) (λ_{ex} = 330 nm). The inset shows the photographs of the solution of **TPEP5** and **G1** in the (B) absence and (C) presence of adiponitrile (20.48 mM) under UV light (365 nm) illumination at 298 K. (b) The plot of fluorescence intensity against the concentration of **G3**.

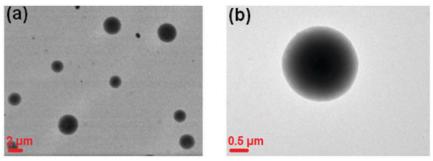

Fig. 4 TEM images: (a) TEM image of the **TPEP5**⊃**G1** complex; (b) enlarged TEM image of (a). Samples were prepared by placing one drop of the $CHCl_3$–acetone solution of the mixtures of **TPEP5** with 4 equiv. of **G1** onto a carbon-coated copper grid.

aggregates was about 2 μm in diameter (Fig. S33, ESI†), which is in good agreement with the above TEM results. Therefore, the above results further confirmed the formation of large sized supramolecular aggregates *via* host–guest recognition-mediated cross-linking.

In summary, a novel TPE-functionalized pillar[5]arene (**TPEP5**) was successfully synthesized by incorporating four pillar[5]arene groups onto the periphery of TPE through the alkyne–azide click reaction. The formation of the **TPEP5**⊃**G1** (1 : 2 molar ratio) supramolecular inclusion complex based on host–guest interactions led to the effective aggregation of **TPEP5**, resulting in the "turn-on" of fluorescence emission based on the AIE mechanism. Moreover, fluorescence "turn-off" could be observed upon further addition of adiponitrile due to the competitive host–guest complexation. In addition, DLS and TEM images confirmed the formation of large sized spherical aggregates due to the host–guest recognition-induced cross-linking. Therefore, this novel supramolecular system offers a new opportunity for the fabrication of novel types of pillararene-based AIE luminogens. Future work will focus on the design and synthesis of highly efficient and selective pillararene-based functional AIE materials.

We are grateful for the financial support from the National Basic Research Program of China (2014CB846000) and the National Natural Science Foundation of China (No. 91227106 and 21202083).

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