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A macrocyclic 1,4-bis(4-pyridylethynyl)benzene showing unique aggregation-induced emission properties†

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A box-like macrocycle based on 1,4-bis(4-pyridylethynyl)benzene was derived in high yield. The macrocyclic fluorogen shows unique aggregation-induced emission properties.

Organic luminogens showing aggregation-induced emission (AIE) properties have attracted great attention in fundamental research and practical applications.[1,2] More and more AIE-active molecular systems have been developed to serve different requirements. For example, AIE-active molecules have been encaged into host–guest supramolecular assemblies and these systems show promising performance in molecular recognition and chemo- and bio-sensing.[3,4] A general strategy to construct such kinds of intriguing structures is to covalently link an AIE-active moiety to the host or guest molecule, the host–guest interaction triggers the emission of the AIE moiety. Normally, an AIE-active moiety is composed of a conjugated center and multiple peripheral phenyl groups, which are linked to the center through a single bond. The activated rotations and vibrations (such as wiggling and scissoring) of the peripheral phenyls around the center exhaust the excitation energy; thus the emission is quenched when the AIE-active moiety is in a free state (gas or in dilute solution). According to the RIM (restriction of intra-molecular motion) mechanism of AIE activity, the emission quenching channels are closed and the AIE-active moiety becomes emissive if the rotations and vibrations are restricted.[1] Rationally, emission turn-on or enhancement can be expected if the host–guest interaction can induce the RIM processes.

Another strategy is to directly use an AIE-active moiety as a guest. Once the guest is encaged into the host and the RIM process occurs, the emission from the AIE-active guest can be turned on. Huang and colleagues implemented this strategy in their pillar and auxiliary supramolecular systems.[2c,5,6] The AIE activity of the reported assemblies, on one hand, provides a novel methodology for signaling the self-assembling process, and, on the other hand, endows the assemblies with unprecedented dynamic fluorescence properties. But the AIE-active moiety has never been used as the host. Recently, Dincă and other groups reported the incorporation of AIE-active moieties into metal–organic frameworks (MOFs).[7–9] In these constructions, the frameworks rather than the AIE-moieties play the role of a host. The development of AIE-active hosts is still an untouched field. Here, we report our work on the construction of an AIE-active macrocycle. It has a box-like structure and contains 1,4-bis(4-pyridylethynyl)benzene building elements, which contribute AIE properties to the whole system.

The synthetic route to the target macrocyclic compound is shown in Scheme 1, and the detailed experimental procedures and the structural characterization data for intermediate **1** and the final resultant are provided in the ESI† (Fig. S1–S7). In brief, Sonogashira coupling reaction of 4-iodopyridine with 1,4-diethynylbenzene efficiently afforded 1,4-bis(4-pyridylethynyl)benzene (BisPy) in a yield of 88%. By using 1,4-dibromomethyl benzene as a quaternizing agent and $[PF_6]^-$ as a counterion, intermediate **1** was obtained in a unit yield. Locking intermediate **1** with BisPy benzene and exchanging Br anions with $[PF_6]^-$, the macrocyclic Box was derived in a good yield of 67%. The characterization data (spectroscopic analyses, FT-IR, NMR and HRMS, ESI†) confirmed the expected structure. It is noted that both Sonogashira coupling and quaternization reactions are highly efficient and can be carried out under mild conditions, thus the macrocyclic compound can be produced in high yield.

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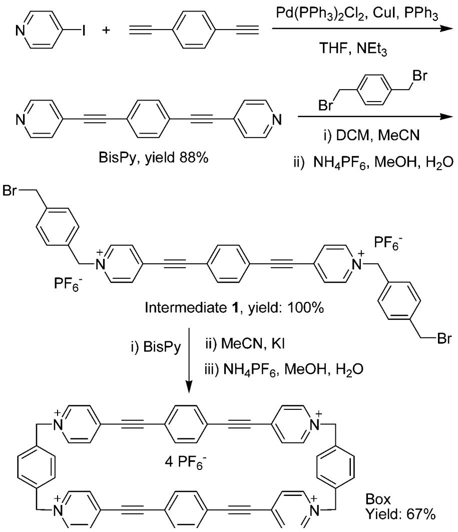
† Electronic supplementary information (ESI) available: Synthesis procedures and characterization data; absorption and emission spectra for Box and **M1**, and $[Box][PF_6]_2Br_2$ and **M1**; and SEM and TEM images of the particles of Box and **M1**. CCDC 1423659. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc02851a



Scheme 1 Synthetic route to the box-like macrocycle containing 1,4-bis(4-pyridylethynyl)benzene moieties.

The emission behavior of the obtained macrocycle was evaluated by the measurement of its fluorescence efficiency (Φ_F) in different states. Using an integrating sphere technique, Φ_F of the powder sample was measured to be 3.2% and the emission maximum appears at around 480 nm. In dilute dimethyl sulfoxide (DMSO) solution (10 μM), Box emits deep blue fluorescence with an emission peak at around 430 nm and its Φ_F is about 1.5% when 9,10-diphenylanthracene was used as a standard. The efficiency decrease observed here and the emission behavior we observed for a 1,2-diphenyl-acetylene derivative suggest that Box may be a molecule with the aggregation-induced emission enhancement (AEE) property, a special case of AIE.[10]

To check the above deduction, we examined the emission response of Box in DMSO solution to the addition of water. Water is a bad solvent for Box and adding an appropriate amount of water into the solution will cause aggregate formation, which allows us to monitor the changes in emission behaviors. The experimental results are shown in Fig. 1A. Keeping the concentration of Box constant, the emission intensity increases continuously with increasing water fraction (f_W, by volume) in solution. This is a representative AEE phenomenon and the quantitative estimation of the fluorescence enhancement is demonstrated in Fig. S8–S11 (ESI†). To assess the AEE behavior, Φ_F was used in the analysis and the data are displayed in Fig. 1B. Φ_F was 1.70% when 10% water was introduced into the solution and it increased to 15.4% when f_W was up to 90%. When f_W was further increased to 95% and 99%, the emission intensity showed little enhancement (Fig. S11, ESI†), and the quantum efficiency was not determined for the partial precipitation in the emission measurement. The aggregate or particle formation was confirmed by the experimental results of dynamic light scattering (DLS) analysis (Table S1, ESI†), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. S12 and S13, ESI†).

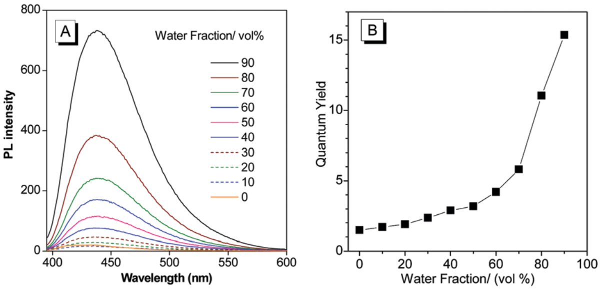


Fig. 1 (A) Photoluminescence (PL) spectra of the box-like macrocycle (Box) in DMSO/H_2O mixtures with different water fractions (f_W, by volume). (B) Changes in the fluorescence quantum yield (Φ_F) of Box in DMSO/H_2O mixtures with f_W. Excitation wavelength (λ_{ex}) = 375 nm. Box concentration = 10 μM.

In comparison with other representative AIE molecules (*e.g.* silole and tetraphenylethene or TPE derivatives), the emission behaviors of Box exhibit its uniqueness. Firstly, the fluorescence quantum yield of the powder Box sample (Φ_F = 3.2%) is evidently lower than Φ_F measured in the DMSO/water mixture solvent at an f_W of 90% (Φ_F = 15.4%) and slightly higher than that measured in the pure DMSO solution (Φ_F = 1.5%). However, for typical AIE and AEE molecules, Φ_F of the solid is much higher than that of the dilute solution, and largely equal to or even higher than that of aggregates formed in mixture solvent with high non-solvent fractions. Secondly, there is not a clear inflection point on the plots of Φ_F *vs.* f_W and relative fluorescence intensity ($I/I_0 - 1$) *vs.* f_W (Fig. 1B and Fig. S9, ESI†). In contrast, for the known AIE and AEE molecules, the plots of Φ_F *vs.* f_W and ($I/I_0 - 1$) *vs.* f_W always show an inflection f_W value (threshold), at which the emission is turned-on due to the formation of aggregates. When f_W is lower than the threshold, no aggregates have been formed; thus no emission enhancement can be observed.

To explain the peculiar phenomenon, the geometric structure of Box was optimized by using DFT simulations (B3LYP, 6-31++G*(d,p)),[11] and we can see that the Box takes a pseudo-rectangle geometry, in which the two 1,4-bis(4-pyridylethynyl)-benzene units are bent from planar due to both ring tension and electrostatic repulsion. The bending angles for α and β are about 156° and 102°, respectively (Fig. 2A). Based on the calculation results and the radii of H, C, N, F, and P atoms, geometric illustrations of Box in different environments are depicted in Fig. 2B–F. In dilute DMSO solution, Box is solvated and the rotations of the phenyl and pyridyl moieties are free (Fig. 2C). According to the RIM mechanism, Φ_F of the Box is low in this case.

But why have we observed a low Φ_F in the solid state of Box? As indicated in Fig. 2A and B, the size of $[PF_6]^-$ is quite large and the four $[PF_6]^-$ anions cannot be accommodated inside the Box but can only be standing outside of the Box and beside the positively charged pyridinium moieties. The rotations of the phenyl and pyridyl moieties become allowable because the large $[PF_6]^-$ anions and the two 1,4-dimethylbenzene units in the two short frames of offer sufficient space. Consequently, Box exhibited quite a low Φ_F in the solid state, which is comparable

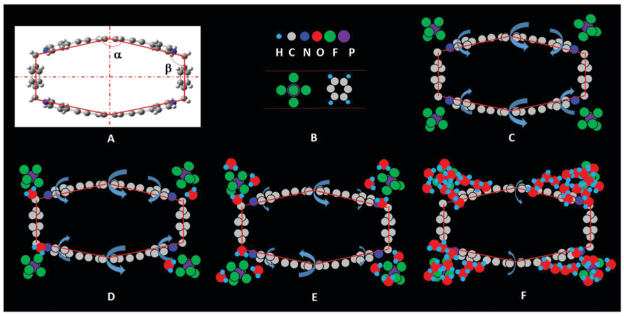


Fig. 2 (A) Optimized geometric structure of the Box, $\alpha = 156°$, $\beta = 102°$. (B) Illustration of the relative size of H, C, N, O, F, and P atoms and the dimensions of the $[PF_6]^-$ anion and the phenyl group. (C–F) Cartoons showing a Box molecule in different cases: (C) in dilute DMSO solution, the solvent molecules are omitted; (D)–(F) in DMSO/water mixtures with small, moderate and high f_W values. In the case of high f_W, water clusters formed by H-bond interaction, they localized around the $[PF_6]^-$ anions and pyridinium cations due to the hydrophilic interaction (F). For the solid powder, the geometric picture is similar to (C), but without solvent molecules. For all cartoons, the size of the curved arrows proportionally indicates the degree of intramolecular rotations; the H-atoms are omitted except in water molecules.

to the case in dilute DMSO solution. As pertinent evidence, when two large $[PF_6]^-$ anions were exchanged with smaller Br^- anions (Scheme S2, ESI†), the space should be contracted somewhat. As a result, the emission efficiency of the solid sample of $[Box][PF_6]_2Br_2$ is 4.0%, a little higher than the Box (3.2% for $[Box][PF_6]_4$).

When water was introduced into DMSO solvent, it is rational to conceive that the H_2O molecules tend to attach to the $[PF_6]^-$ anions and pyridinium cations. H_2O molecules easily form clusters *via* a hydrogen bond (H-bond). Such an event of cluster binding hampers the free rotation of the pyridinium moieties. As a result, the emission is enhanced and Φ_F increased. When f_W is relatively low, the H_2O molecular cluster bonding to the $[PF_6]^-$ anions and pyridinium cations is relatively small and the restricted rotations occur around the pyridinium moieties and the restriction is not strong. In these cases, the system showed weak emission enhancement (Fig. 2D and E). While at high f_W, large H_2O molecular clusters constructed by H-bond networks nearly envelop the pyridinium cations and $[PF_6]^-$ anions and partial of the phenylethynyl moieties (Fig. 2F). The heavily restricted intramolecular rotations greatly boost the emission. Therefore, a high Φ_F has been recorded in DMSO/water mixture solvents with high f_W (*e.g.* 90%).

To support the above explanation, we synthesized a model compound **M1**, which is a simple linear structure containing a 1,4-bis(4-pyridylethynyl)benzene fluorophore (see the inset of Fig. 3B). The characterization data are presented in the ESI† (Fig. S14–S17, ESI†). In pure DMSO, **M1** emits weak fluorescence with a Φ_F of 0.5% (Fig. 3A and B). When f_W increases to 90%, a large increase can be observed in an exponential way for both the emission intensity and Φ_F (13.2%), more than 26 times that in dilute DMSO solution (ref. Fig. S18 and S19, ESI† for the absorption and emission properties of **M1**). As **M1** is insoluble in water, severe aggregation has occurred, as revealed by the data of dynamic light scattering and the obtained transmission electron microscopy (TEM) image at an f_W of 90% (Fig. S20 and S21, ESI†). In the solid powder sample, **M1** emits moderate fluorescence with a Φ_F of 14.0% (Fig. 3B). These data indicate that **M1** is a typical AEE molecule. The solid state emission of **M1** (Φ_F = 14.0%) is drastically different from that of Box (Φ_F = 3.2%). This difference can be understood from the single crystal data of **M1** (CDCC 1423659). As shown in Fig. 3C, the large $[PF_6]^-$ anions stand by the linear-shaped **M1** molecules rather than insert between them. Meanwhile, without the formation of the macrocycle, the ending phenyls in the adjacent **M1** molecules form C–H···π bonds with the central phenyl groups (d = 2.284 Å, Fig. 3D), which stabilize the solid structure and restrict the intramolecular rotations. According to the RIM mechanism, **M1** should have a high Φ_F value in the solid state.

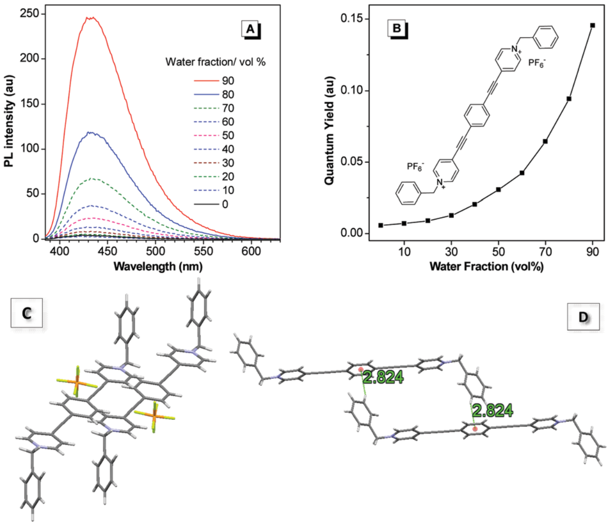


Fig. 3 (A) Photoluminescence (PL) spectra of M**1** in DMSO/H_2O mixtures with different water fractions (f_W, by volume). (B) Changes in the fluorescence quantum yield (Φ_F) of M**1** in DMSO/water mixtures with f_W. λ_{ex} = 375 nm. M**1** concentration = 10 μM. (C) A side view of M**1** molecular packing, which shows two $[PF_6]^-$ anions standing by the molecular pair. (D) Another side view of molecular packing in the M**1** crystal, indicating the C–H···π bonds between the ending and central phenyl groups in the adjacent M**1** molecules (d = 2.284 Å).

The Box, a hollow macrocyclic compound featuring AEE properties, gives new insights into the research area of AIE and AEE materials. The emission enhancement of the macrocyclic fluorophore is induced by the formation of non-solvent clusters surrounding the rotors but not by the formation of fluorophore aggregates. By introducing tetrakis-carboxylic modified tetraphenylethene (TPE, a representative AIE-active luminogen) into MOFs, Dincă *et al.* demonstrated the matrix coordination induced emission effect.[7] Despite the large interchromophore distances imposed by the coordination to metal cations, the fluorescence of the individual TPE derivative was turned-on by coordination ligation in the porous matrix. In the present case, the interaction between water clusters and $[PF_6]^-$ anions and pyridinium cations plays the role of coordination ligation. This observation is meaningful, although the interaction is not as strong as that of metal cations and carboxylic groups. Recently, a similar emission behavior was observed in organic dyes with excited-state intramolecular proton transfer (ESIPT) properties. Emission can be enhanced in protonic solvents (*e.g.*, methanol and water), where the proton of methanol can form a hydrogen bond with the ESIPT dye and possibly form solvent clusters surrounding the dye molecule, thus enhancing its light emission.[12]

In summary, we have derived a hollow macrocyclic compound (Box) through an efficient synthetic route. The total yield of a four-step reaction is about 60%. The Box demonstrates peculiar emission behaviors. It is weakly emissive in dilute DMSO solution (Φ_F = 1.5%), while the emission becomes evidently stronger in DMSO/water with a high water fraction (Φ_F = 15.4% at f_W = 90%). In this aspect, Box possesses a typical AEE (a special case of AIE) property. But Φ_F decreases to 3.20% in the solid powder. Meanwhile, there is not a clear inflection point on the plot of Φ_F *vs.* f_W (also true for $(I/I_0 - 1)$ *vs.* f_W). By carefully analyzing the geometric structure of Box, we associated these peculiar emission behaviours with the formation of water clusters around the $[PF_6]^-$ anions and pyridinium cations in DMSO/water mixtures, which hinder the free rotations of the phenyl and pyridyl groups of Box and thus trigger the emission of the 4-bis(4-pyridylethynyl)benzene fluorophore. In the solid powder, the large volume of the four $[PF_6]^-$ anions and the two benzyl groups hold enough free space for the rotations of the phenyl and pyridyl groups, thus the emission of Box is quenched. These deductions are in good agreement with the RIM mechanism and have been supported by the AEE performance of the model compound **M1**. It is expected that molecules in a size that is suitable for the vacant may turn on the emission of the Box, and the macrocyclic AIE fluorogen can find application in fabricating novel and emissive supramolecular structures.

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