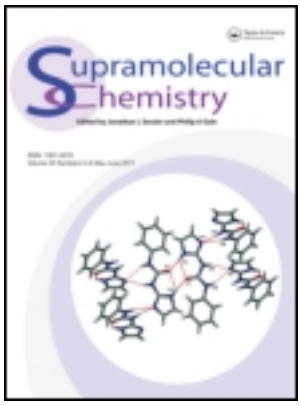

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Reversible solubilisation through hydrogen-bond-mediated assembly

Fan Gao [a], Yichen Tan [a], Yue Yu [a], Hao Chen [a] & Yuguo Ma [a]

[a] Beijing National Laboratory for Molecular Sciences (BNLMS), Key Lab of Polymer Chemistry & Physics of Ministry of Education, College of Chemistry, Peking University, Beijing, 100871, P.R. China

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Reversible solubilisation through hydrogen-bond-mediated assembly

Fan Gao, Yichen Tan, Yue Yu, Hao Chen and Yuguo Ma*

Beijing National Laboratory for Molecular Sciences (BNLMS), Key Lab of Polymer Chemistry & Physics of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, P.R. China

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A novel approach was developed to improve the solubility of non-soluble compounds by introducing solubilising molecules peripherally through hydrogen-bond-mediated assembly. The solubilisation process can be reversed by adding competing hydrogen bonding moieties and removing the solubilising molecules. This method may potentially facilitate device fabrication.

Keywords: solubilisation; hydrogen bond; truxene; device fabrication

Introduction

For large-scale and efficient processing of organic/polymer materials, such as in the manufacture of organic light-emitting diodes (OLEDs), organic photovoltaic cells and organic field-effect transistors, the solubility of the organic compounds is a critical issue (*1–6*). The insolubility leads to difficulties in purification, characterisation and device fabrication; thereby hindering the application of many molecules with good photoelectronic properties. For example, shape-persistent π-conjugated molecules have been extensively studied, due to their prominent absorption or emission properties as well as the energy and charge transfer abilities. However, the rigidness of the planar molecular structures often results in poor solubility in common volatile solvents. To solubilise these molecules is the premise of solution processing such as drop casting (*7*, *8*) and spin coating (*1*, *3*, *4*, *9*), which leads to low-cost, high-volume, large-area applications and commercialisation (*10*). Covalent incorporation of alkyl chains at the periphery is a common way to improve the solubility in a non-polar solvent (*11*, *12*). But it often requires additional synthetic effort and leads to disturbances of the orderly aggregation or photophysical properties of the molecules. In addition, the solubility of such modified molecules is less tunable and the 'solubilisation' is irreversible.

Non-covalent functionalisation is another strategy for solubilisation. It is reversible and has fewer disturbances on the original molecules. For example, single-wall carbon nanotubes have been functionalised non-covalently by aromatic compounds, conjugated polymers and biomacromolecules, through π–π stacking or hydrophobic interactions (*13–16*). In these approaches, non-covalent modifications improve the solubility remarkably without compromising the properties of the original molecules. Hydrogen bond is a well-investigated and widely applied secondary interaction in supramolecular chemistry. It has medium strength and is tunable over a wide range of association energies, around 4–120 kJ/mol. Various assembling structures based on hydrogen bonding have been developed and they are responsive to external stimuli due to the reversible nature of such non-covalent interaction (*17–19*). In particular, Zimmerman's group used hydrogen bond to 'cross-link' two normally immiscible polymers, and the hydrogen bonding interaction makes the two polymers miscible (*20*). Similar methods may be extrapolated to the solublisation process. Indeed, hydrogen-bond-mediated assembly can cause the change in solubility (*21*).

In this contribution, we introduce a novel approach to improve the solubility of an example of shape-persistent π-conjugated molecules. Similar to the solubilising processes with surfactants or dispersing agents, the primary molecule can be dissolved through the formation of supramolecular assembly with complementary hydrogen bonding groups that associate peripherally with solubilising alkyl chains. Because the bonding is non-covalent, this method is highly tunable. It is convenient to adjust solubility by changing the amount of the solublising molecules or by changing the length and constitution of the alkane chains. The primary molecule can also be dissolved in different solvents by simply changing the solubilising molecules. Moreover, this solubility-improving process can be reversed by removing the solubilising molecules from the supramolecular assembly with primary molecules through, for example adding competitive hydrogen bonding moieties of the solubilising molecules.

*Corresponding author. Email: ygma@pku.edu.cn

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Result and discussion

Design

To illustrate this method, we chose primary molecule **1** and solubilising molecule **2** (Figure 1). Molecule **1** contains a 10,15-dihydro-5H-diindeno-[1,2-a:1′,2′-c]fluorine (truxene) core and three diaminothio-triazinone groups at its periphery. It was derived from a series of truxene-based molecules that have been extensively investigated as blue light emitting OLED materials (*22*, *23*), light harvesting materials (*24*), two-photon absorption materials (*9*) as well as building blocks for constructing dendrimer (*22*–*24*) or star polymer structures (*9*, *25*). The unique structure provides it with the potential to be used in molecular electronics, photoelectronics and other applications.

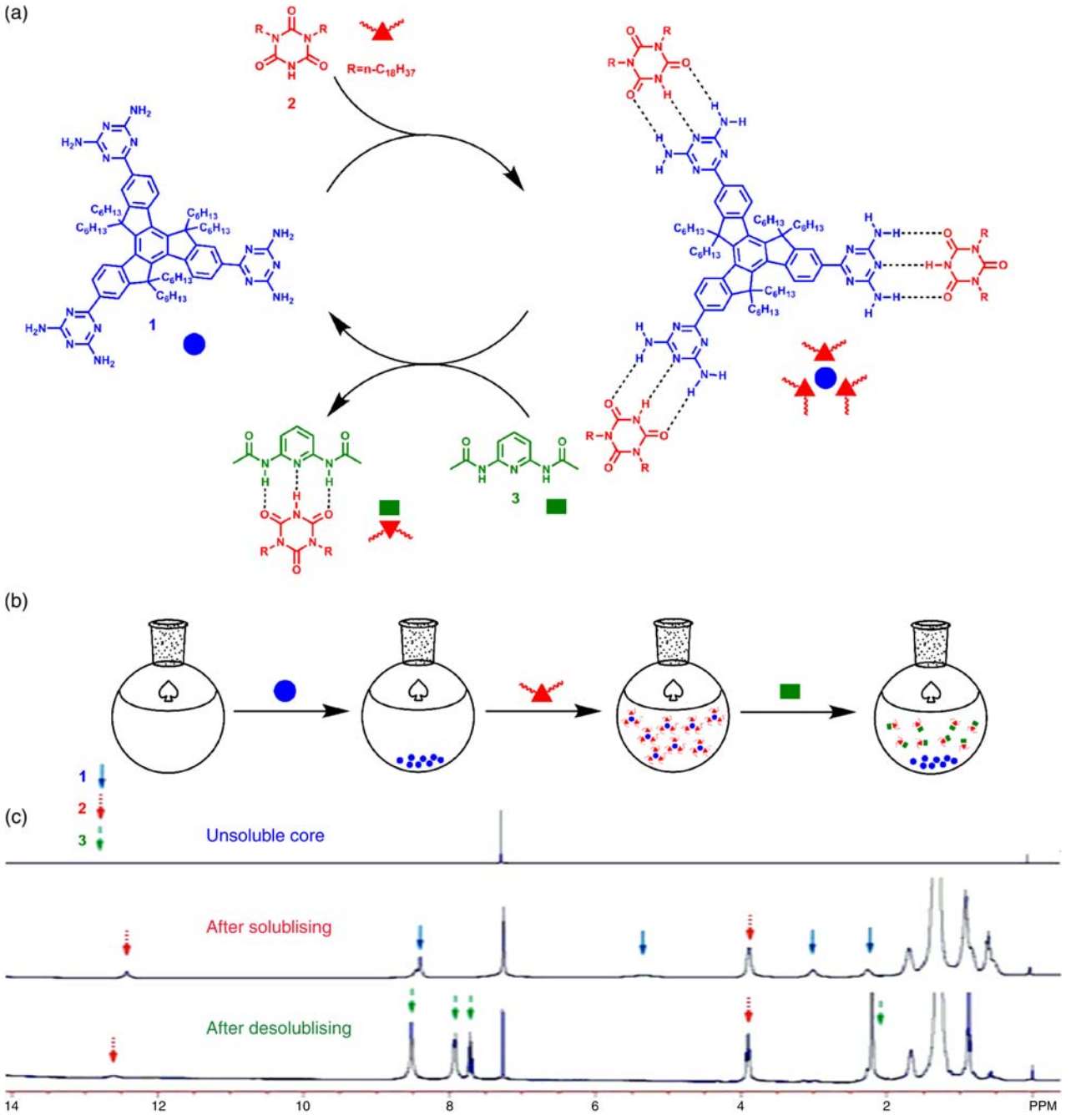
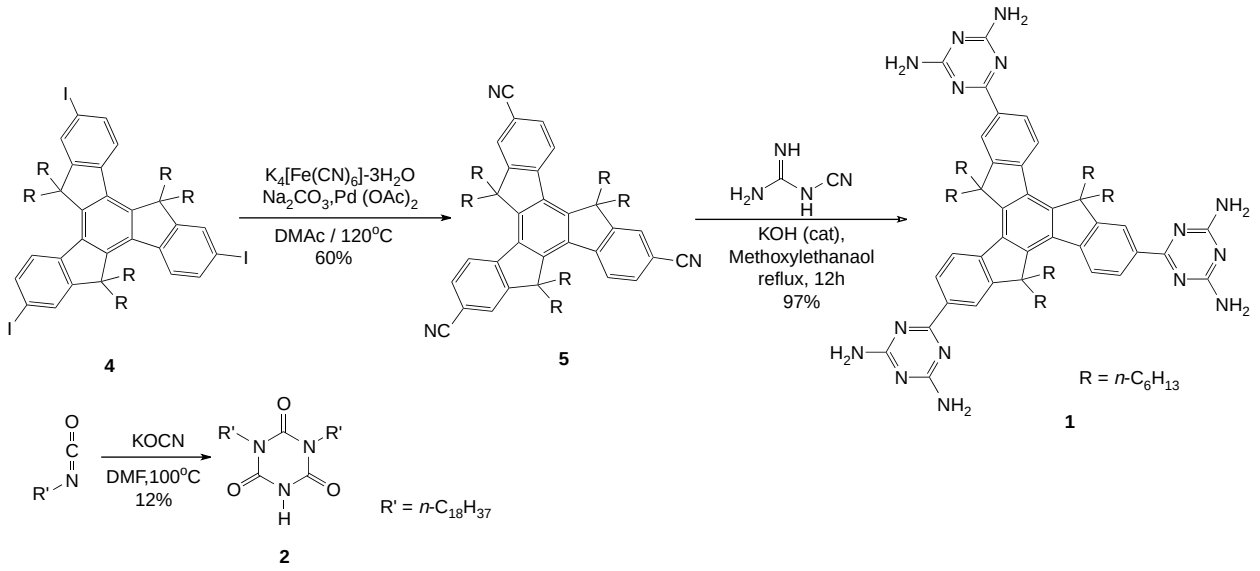


Figure 1. (a),(b) The schematic representation of solubilising and desolubilising processes: **1** was not soluble in chloroform; after adding **2**, the 1:3 assembly of **1** and **2** dissolved; **1** precipitated after **3** was added. (c) The solubilising and desolubilising processes monitored by ^{1}H NMR: the blue, red and green arrows assign the resonance signal of **1**, **2** and **3**, respectively. The concentration of **1** is 1×10^{-2} mol/l.



Scheme 1. Synthesis of molecules **1** and **2**.

Peripherally furnished diaminothio-triazinone group is a triple hydrogen bond motif with donor-acceptor-donor (DAD) sequence. Molecule **2** is an alkyl-substituted cyanuric acid, which contains a triple hydrogen bond motif with acceptor-donor-acceptor (ADA) sequence. These two hydrogen-bond motifs have complementary sequences like the well-studied melamine-cyanuric acid system (*8*, *26–28*). As shown in Figure 1(a), molecules **1** and **2** can assemble through the DAD—ADA triple hydrogen bond with a 1:3 ratio.

Synthesis

Scheme 1 illustrates the synthetic routes of molecules **1** and **2**. The synthesis of **1** started from a reported compound, iodinesubstituted hexyl-truxene **4** (*29*). Reaction of this iodo-truxene with $K_4[Fe(CN)_6]$ with the $Pd[OAc]_2$ catalyst formed cyanotruxene **5** (*30*), which further reacted with cyanoguanidine to afford molecule **1** (*31*). Molecule **2** was synthesised by the cyclisation of alkyl-isocyanate and potassium cyanate (2:1) according to the literature (*32*).

^{1}H NMR study of assembly

In the ^{1}H NMR spectra (Figures 1(c) and 2(a)), only insignificant signal was observed from a suspension of **1** in $CDCl_3$, because molecule **1** is barely soluble in chloroform. However, when molecule **2** was added into the suspension, **1** began to solubilise, and the resonance signal of **1** was observed in the ^{1}H NMR spectrum, including the

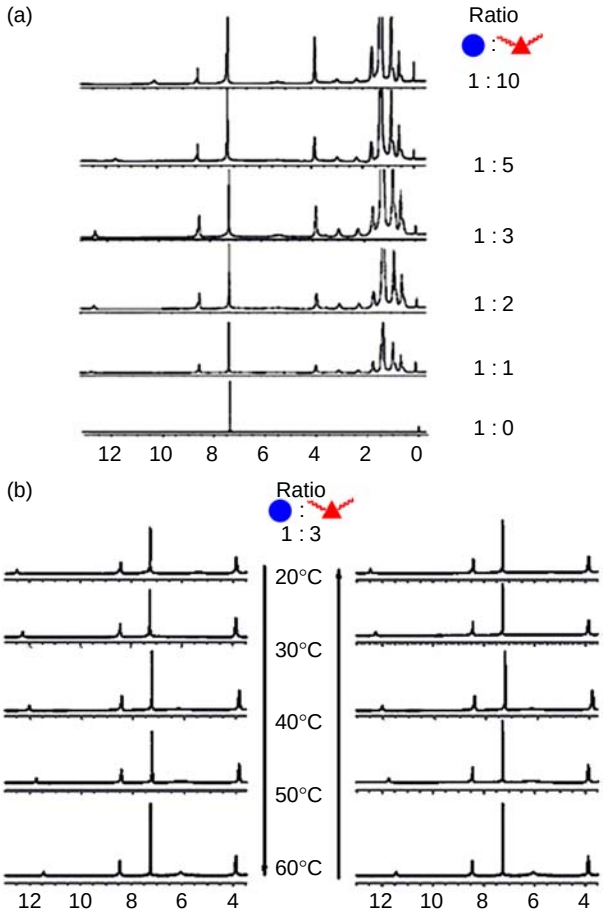


Figure 2. ^{1}H NMR (300 MHz) spectra of the mixture of **1** and **2** in $CDCl_3$ at (a) different ratios at 25°C and (b) different temperatures. The concentration of **1** is 1×10^{-2} mol/l.

8.5 ppm peak corresponding to the nine aromatic protons, the broad peak at 5.4 ppm corresponding to the NH_2 protons, as well as the 3.0 and 2.2 ppm peaks corresponding to the 12 CH_2 protons close to the truxene core. We also observed a broad resonance peak at 12.5 ppm, which corresponded to the NH proton of molecule **2**. The downfield shift from the expected imide NH proton signal at around 8.5 ppm indicated the formation of the hydrogen bonds. As the molar ratio of molecules **2** to **1** increased from 1:1 to 3:1, molecule **1** was completely dissolved and the intensity of the resonance signal enhanced. Further addition of **2** did not lead to a stronger signal of **1** and the NH proton resonance signal began to shift upfield, indicating that in this hydrogen bonding complex, the ratio of **1** and **2** was 1:3. It was consistent with the theoretical stoichiometric ratio of the two compounds. The free NH groups in excess of molecule **2** have lower chemical shift in ^{1}H NMR than the NH groups involved in the formation of hydrogen bonds. Because of the fast exchange between the two kinds of NH groups, the resonance peak at 12.5 ppm moved upfield.

We next investigated the thermo-stability of the hydrogen bonding complex by conducting ^{1}H NMR experiments at various temperatures. As shown in Figure 2(b), the resonance peak at 12.5 ppm shifted upfield to 11.5 ppm as temperature was increased from 20 to 60°C, indicating the disassembling of the hydrogen bonding complex. However, compared with the resonance peak of free NH group at *ca*. 8.5 ppm, it was still quite downfield shifted, suggesting that the hydrogen bonding complex was only disassembled partially. This disassembling process was reversible, as indicated by the reappearance of the resonance peak at 12.5 ppm once the temperature was decreased back to 20°C. Adding competing molecules can also disassemble the 1:3 hydrogen bonded complex of **1** and **2** (Figure 1(a,b)). We chose 2,6-diacetyldiaminopyridine (**3**) as competing molecule since it contains the same DAD hydrogen bonding sequence as molecule **1**. Therefore, it can replace molecule **1** and form 1:1 hydrogen bonding complexes with the solubilising molecule **2**. When **3** was added into the solution of the 1:3 hydrogen bonding complex of **1** and **2**, the solution became turbid. By adding excess of **3**, most of molecule **1** was precipitated. As shown in the ^{1}H NMR spectrum (Figure 1(c)), the resonance signal of molecule **1** decreased significantly when excess amounts of molecule **3** was added, which was consistent with the precipitation phenomena. Through simple filtration and washing with chloroform, we could recycle molecule **1**.

Optical properties

The UV–vis absorption spectra and normalised fluorescence emission spectra (Figure 3(a)) of molecule **1** and the hydrogen bonded assembly were almost identical at the concentration of 5×10^{-6} mol/l. Because the solubility of **1** was poor, no emission spectrum was obtained at higher concentration or in thin film. On the other hand, only a slight red shift was observed in the normalised fluorescence emission spectra of the hydrogen bonded assembly at higher concentration or in thin film (Figure 3(b)). This indicated that the optical property of molecule **1** was not affected by the formation of hydrogen-bond-mediated complex. Therefore, the solubilisation process would not compromise the application of the primary molecule in photoelectronics or fluorescence sensing.

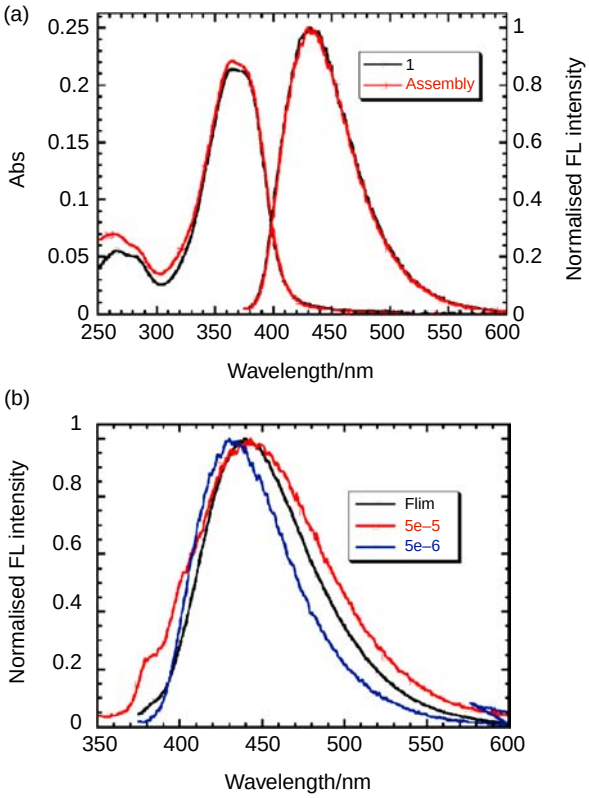


Figure 3. (a) UV–vis absorption spectrum and normalised fluorescence emission spectrum of **1** and the assembly in chloroform at the concentration of 5×10^{-6} mol/l; (b) the normalised fluorescence emission spectra of the hydrogen bonded assembly at the concentration of 5×10^{-5} mol/l, 5×10^{-6} mol/l and in thin film.

Conclusion

In conclusion, a reversible, non-covalent 'solubilisation' method is presented in this contribution. A non-soluble fluorescent molecule was solubilised through the formation of hydrogen-bond-mediated assembly and was desolubilised by adding competing moieties to break the assembly. The solublising and desolublising processes were monitored by the ^{1}H NMR spectrum. This method improved the solubility of the primary molecule without affecting its photoluminescence spectra and photoelectronic properties.

Therefore, it could serve as a general solubilising method, which might potentially facilitate the photoelectronic device fabrication. Further investigation will focus on introducing other functional groups onto the primary molecule with this method.

Experimental

3,8,13-Triiodine-5,5′,10,10′,15,15′-hexahexyltruxene (**4**) was synthesised according to the literature (*29*). DMF was dried over $MgSO_4$ and distilled under reduced pressure. All other reagents and solvents used in the synthesis were purchased from commercial suppliers and used without further purification. Chloroform used in absorption and photoluminescence spectra was distilled over CaH_2.

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-300 (300 MHz) spectrometer. Elemental analysis was carried out using an Elementar VARIO EL elemental analyser. Absorption spectra were recorded on a Perkin-Elmer Lambda 35 UV–vis spectrometer. Photoluminescence spectra were recorded on a Perkin-Elmer LS55 luminescence spectrometer.

3,8,13-Tricyano-5,5′,10,10′,15,15′-hexahexyltruxene (5)

A flask was charged with **4** (2.21 g, 1.80 mmol), *N*,*N*-dimethylacetamide (100 ml), $K_4[Fe(CN)_6]\cdot 3H_2O$ (530 mg, 1.20 mmol), sodium carbonate (570 mg, 5.40 mmol, 3.0 equiv.) and $Pd(OAc)_2$ (0.5 mol%). The flask was evacuated and filled with nitrogen twice and heated to 120°C. The conversion was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and diluted with 100 ml of EtOAc. The resulting slurry was filtered and the filtrate was washed with water and 5% NH_4OH and then dried over Na_2SO_4. After the solvent was removed *in vacuo*, the residue was purified by flash column chromatography (PE/EtOAc = 20/1) to afford **5** as a yellow solid (1.02 g, 60%). ^1H NMR (300 MHz, $CDCl_3$) δ 8.43–8.46 (3H, d, $J = 8.5$ Hz, Tr-H), 7.77–7.73 (3H, s, Tr-H), 7.77–7.73 (3H, d, $J = 8.5$ Hz, Tr-H), 2.78–2.96 (6H, m, CH_2), 1.96–2.13 (6H, m, CH_2), 0.79–1.03 (36H, m, CH_2), 0.60–0.70 (18H, t, $J = 7.2$ Hz, CH_3), 0.38–0.57 (12H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.0, 148.1, 143.5, 137.5, 130.7, 125.9, 124.9, 119.3, 110.4, 56.3, 36.6, 31.3, 29.1, 23.8, 22.1, 13.8; anal. calcd for $C_{66}H_{87}N_3$:C, 85.94; H, 9.51; N, 4.56. Found: C, 86.08; H, 9.29; N, 4.13.

6,6′,6″-(5,5′,10,10′,15,15′-Hexahexyltruxene-3,8,13-triyl)tris (1,3,5-triazine-2,4-diamine) (1)

A mixture of **5** (1.02 g, 1.11 mmol), dicyandiamide (0.93 g, 11.1 mmol) and powdered KOH (0.12 g, 2.1 mmol) in 2-methoxyethanol (60 ml) was heated at reflux for 24 h. The mixture was then cooled and the volatiles were removed *in vacuo*. Recrystallisation of the residue from DMF—MeOH afforded pure **1** as a yellow solid (1.27 g, 97%). ^1H NMR (300 MHz, DMSO-d_6) δ 8.44–8.47 (3H, d, $J = 7.9$ Hz, Tr-H), 8.34–8.38 (3H, s, Tr-H), 8.34–8.38 (3H, d, $J = 7.9$ Hz, Tr-H), 6.80 (12H, s, $-NH_2$), 2.98–3.04 (6H, m, CH_2), 2.10–2.13 (6H, m, CH_2), 0.79–1.03 (36H, m, CH_2), 0.60–0.70 (18H, t, $J = 7.2$ Hz, CH_3), 0.38–0.57 (12H, m, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ 170.3, 167.5, 153.0, 146.0, 142.3, 137.9, 135.6, 126.7, 124.0, 121.4, 55.4, 38.7, 36.3, 31.1, 28.8, 23.6, 21.6, 13.6.

1,3-Dioctadecyl-1,3,5-triazinane-2,4,6-trione (2)

A mixture of potassium cyanate (0.215 g, 2.65 mmol), octadecyl isocyanate (1.47 g, 5.0 mmol) and dry DMF was stirred at 100°C for 24 h. The cooled reaction mixture was filtered. The filtrate was concentrated by removing the solvent *in vacuo* and the residue was stirred with distilled water for 2 h (60°C) and then acidified with concentrated aqueous HCl. The mixture was filtered and the slurry was extracted by $CHCl_3$ (three times). The organic layers were combined and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was treated with CH_2Cl_2. The undissolved substance was collected by filtration and recrystallised with hexane to afford **2** as a white solid. (0.19 g, 12%) ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (1H, s, NH), 3.83–3.88 (4H, t, $J = 7.5$ Hz, CH_2), 1.61–1.65 (4H, m, CH_2), 1.24–1.26 (60H, m, CH_2), 0.86–0.90 (3H, t, $J = 6$ Hz, CH_3).

Preparing samples for ^1H NMR study

The $CDCl_3$ used in the NMR study was treated with dry Al_2O_3 (basic) to remove acid and water. Molecule **1** (5.9 mg) was suspended in 0.5 ml of $CDCl_3$ and 2.8 mg of **2** was added repeatedly to obtain **1** and **2** solutions in different ratios. Fifteen milligrams of **3** were added to precipitate **1**.

Preparing samples for optical properties study

Molecule **1** (5.9 mg) was dissolved in 0.5 ml of DMSO and diluted with $CHCl_3$ to obtain the solution of **1**. Molecule **1** (5.9 mg) and 8.4 mg of **2** were dissolved in 5 ml $CHCl_3$ and diluted with $CHCl_3$ to obtain the solution of assembly complex at different concentration or drop-casted onto a quartz chip to obtain the thin film.

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