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Organogels formed by substituent-free pyrene-appended oligo(*m*-phenylene ethynylene)s†

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A new class of pyrene-appended *m*-phenylene ethynylene oligomers, which bear no alkyl chains or heteroatoms, have been demonstrated to gelate organic solvents, and one of them forms chiral twisted gels in cyclohexane.

 π -Conjugated low-molecular-mass organic gelators (LMOGs) have received great attention due to their potential applications in biomedical and optoelectronic materials.^{1,2} Typically, the presence of long alkyl chain(s) or steroidal or other non-conjugated unit(s) in the gelator molecules is necessary to facilitate the formation of threedimensional (3D) networks and to promote the aggregation of the whole molecular framework.² However, for the development of LMOGs with optoelectronic properties, which are usually designed on the basis of large aromatic systems, these inactive and isolating groups are undesirable and their introduction also reduces the atom economy of the resulting LMOGs. In the past decade, several kinds of conjugated backbones which bear no aliphatic chains or steroidal units have been reported to gelate organic solvents.³⁻⁹ However, discrete auxiliary polar groups, including cyano and trifluoromethyl,³ amide,⁴ acid,^{5a} amino,^{6a,b} heterocycle,^{4,5a,6b,7,8a} β -diketone-boron difluoride,6a imine,3b ether,8a,b ester9 and imide8b units, have been introduced to enhance the stacking of the designed conjugated cores through electrostatic interaction and/or hydrogen bonding. In one case, the gelation of cyano-bearing stilbene derivatives requires the assistance of additional pyridine-Ag⁺ coordination.^{3f} Herein, we report that, without bearing any polar groups or heteroatoms, pyrene-appended oligo(m-phenylene ethynylene)s are able to gelate organic solvents of low and modest polarity. We further describe that fibres formed by one oligomer exhibit uneven symmetry breaking, leading to the formation of chiral assemblies.

Compounds **1a-1d** and **2a-2c** were designed and synthesized and the synthetic details are presented in the ESI.[†] The pyrene subunit was introduced to all the compounds as a steering stacking subunit,¹⁰ while the oligo(*m*-phenylene ethynylene) chains were explored to see if they could serve as tunable flexible chains for the formation of 3D fibrous networks, as observed for alkyl chains in many reported conventional gelators for the gelation of organic solvents.



The gelation properties of these pyrene derivatives were first investigated by the "stable-to-inversion of a test tube" method in discrete organic solvents. The results are summarized in Table 1. In a typical experiment, one compound was dissolved in an organic solvent by heating at 75 °C. The solution was then allowed to cool down to room temperature under ultrasound. All the compounds could not gelate dichloromethane, chloroform, tetrahydrofuran, 1,4-dioxane or toluene, and most of them, except 2b which partially gelated *n*-hexane, were either insoluble or precipitated in apolar n-hexane or polar acetonitrile or methanol. However, the longest 1d and 2c gelated cyclohexane, decahydronaphthalene, ethyl acetate and acetone as well as the mixtures of dichloromethane with n-hexane and methanol. In all the cases, the critical gelation concentration (CGC) of 2c was lower than that of 1d for the identical solvent, implying that the ethynyl group at the one end of 1d was unfavourable to the gelating process. Compounds 1b and 2b could gelate cyclohexane, whereas 2b could also gelate the 1:1 mixture of dichloromethane and methanol. However, the CGC was pronouncedly higher than that of the respective analogues 1d and 2c, and it took a longer time for the solution of 1b and 2b to realize the solution-to-gel transition. These facts indicate that the longer 3-mer *m*-phenylene ethynylene chain was stronger than the shorter 2-mer chain in providing the gelating ability for both series of compounds. The alcohol precursor for the preparation of 2c,

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Table 1 Gelation properties of compounds $1b-1d,\,2b$ and 2c in organic solvents a

Solvents	1a	1b	1c	1d	2a	2b	2 c
HE	Р	Р	Ι	Ι	Р	PG	I
Cyclohexane	Р	G (4.72)	PG	G (2.56)	Р	G (8.50)	G (1.60)
DHN	S	P	Р	G (4.65)	S	S	G (2.46)
AcOEt	S	S	S	G (21.2)	S	S	G (12.5)
Acetone	S	S	Р	G (11.7)	S	S	G (6.67)
CH_2Cl_2/HE (2:5, v/v)	S	Р	Р	G (8.64)	S	S	G (7.64)
$CH_2Cl_2/MeOH(1:1, v/v)$	S	Р	Р	G (5.86)	PG	G (22.5)	G (3.83)
PhMe	S	S	S	S	S	S	S
CH_2Cl_2	S	S	S	S	S	S	S
CHCl ₃	S	S	S	S	S	S	S
THF	S	S	S	S	S	S	S
1,4-Dioxane	S	S	S	S	S	S	S
MeCN	S	Р	Р	I	Р	S	I
MeOH	Р	Р	Ι	Ι	Р	Ι	Ι

^{*a*} The values in parentheses are the critical gelation concentrations (CGCs) in mg mL⁻¹. HE: *n*-hexane; DHN: decahydronaphthalene; G: gel; I: insoluble; PG: partial gel; P: precipitation; S: solution.

i.e., compound 5 in the ESI,† did not gelate any organic solvents, suggesting that intermolecular hydrogen bonding formed by the hydroxyl group weakened the gelating ability of the conjugated backbone. For comparison with the most efficient gelator 2c, compound 3 was also prepared. It was found that this compound did not gelate any organic solvent, reflecting that the pyrene subunit in 2c played a crucially important role in endowing the backbone with the gelating capacity.



The thermal stability of gels **1b**, **1d**, **2b** and **2c** was also determined by the "stable-to-inversion of a test tube" method. The gel–sol transition temperatures (T_{gel}) ranged from 24 to 43 °C at their respective critical gelation concentrations (Fig. S49a, ESI†). It was noted that the expected higher T_{gel} values of **2c** than those of **1d** were not observed, although **2c** had lower CGCs compared to **1d**. The results indicated that the **1d** gels are more stable than the **2c** gels. Moreover, the plot of T_{gel} as a function of the **2c** gelator concentration showed a nonlinear increase in thermal stability with increasing concentration (Fig. S49b, ESI†).

To investigate the morphologies of the new organogels, airdried samples were subjected to both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses (Fig. 1 and Fig. S50, ESI[†]). It was found that the morphologies of all the xerogels were dependent on the length of the backbone. For example, the SEM images of both **1d** and **2c** in cyclohexane showed that these gelators generated multi-layered entangled 3D networks consisting of bundles of long fibrils, which must be responsible for the observed gelation. Different from those of **1d** and **2c**, the SEM images of shorter **1b** and **2b** in cyclohexane showed broad fibrous networks. The fibres of **1b** are approximately 0.13 µm and that of **2b** are 1.3 µm in width. The TEM pictures also confirmed the above results, but provided even clearer network structures. Interestingly, for the gels of **2c**, obvious chiral twisted



Fig. 1 SEM (a and c) and TEM (b and d) images of air-dried organogels formed in cyclohexane by **2b** (a and b), and **2c** (c and d).

structures were observed from both the SEM and TEM images (Fig. 5, *vide infra*).

The rheological properties of the gels formed by **1d** and **2c** were determined by a frequency sweep test at 20 °C. Both organogels exhibited higher storage modulus (*G'*) values than loss modulus (*G''*) values over the whole scanning frequency range, which is typical for viscoelastic soft solids (Fig. S51, ESI†). The ratio of the storage modulus value to the loss modulus value (*G'/G''*) is in the range of 9–16 for **1d** and 5–9 for **2c**. It suggests that the dissipation of energy is less for the gels of **1d**, thus indicating a stronger network. This result is consistent with those obtained for the T_{gel} .

To get insight into the role of the pyrene subunit in the formation of the gels, we also investigated the spectroscopic properties of compounds **1d** and **2c** in homogeneous solutions. As shown in Fig. 2, **1d** and **2c** gave rise to almost the same UV-visible absorption spectra in cyclohexane. The absorption maxima around 295 nm, 364 nm and 385 nm correspond to the absorptions of the pyrene subunit. The ratio of the intensities I_{385}/I_{295} increases nonlinearly with the increase of the concentration from 1.0 µM to 30 µM at 25 °C. The hyperchromic effect of the absorption centred around 385 nm supports J-type aggregation of the pyrene subunit.¹¹ For comparison, the UV-visible spectrum of controls **3** and pyrene were also recorded in cyclohexane. Within the identical concentration range, the absorption intensity of both compounds was linearly related to the concentration (Fig. S52 and S53, ESI†), suggesting that no aggregation took place.

The fluorescent spectra of **1b–1d** and **2a–2c** were also recorded in cyclohexane at different concentrations (1.0 μ M to 1.0 mM) at 25 °C. For **2c**, two sharp peaks located at 392 nm and 413 nm, respectively, and a shoulder at around 432 nm were detected. Upon increasing the concentration, the sharp



Fig. 2 UV-vis absorption spectra of (a) **1d** and (c) **2c** in cyclohexane at different concentrations and the plots of I_{385}/I_{295} vs. concentration for (b) **1d** and (d) **2c**.

peak at 392 nm faded and red-shifted (for 0.1 mM) or disappeared (for 1.0 mM), while the peak at 413 nm and the shoulder became enhanced (Fig. 3a). Similar results were also observed for other compounds (Fig. S55 and S56, ESI⁺). When the gel of 2c in cyclohexane was formed, the shoulder at around 432 nm became enhanced dramatically and a strong band centered at 484 nm emerged (Fig. 3b), which should reflect the enhanced stacking of the pyrene subunit in the gel state. However, no such emissions were observed in the fluorescent spectra of control 3 in cyclohexane. These results indicate that, compared with 3, all the compounds bearing the pyrene subunit have a higher tendency of stacking.^{11b,12} The fact that the shorter analogues did not gelate organic solvents or just had a low gelating ability suggests that the longer oligo(m-phenylene ethynylene) chain of 1d and 2c also played a key role in enabling the gelating ability by providing additional stacking and holding the 1D aggregates into bundle fibrils (Fig. 4). Thus, to some extent, the function of the aromatic chain is similar to that of long alkyl chains in many reported organogelators.^{1,2}

On the basis of the above experimental observations, we proposed a possible mechanism for the hierarchical self-assembly of the new pyrene-derived conjugated compounds into gels (Fig. 4). In the first stage, the pyrene core stacked into one-dimensional (1D) column-styled aggregates with the assistance of the stacking of the benzene subunits.^{11b,12} Such 1D aggregates further assembled into bundle fibrils, which were stabilized by the stacking of the benzene subunits of the adjacent aggregates. These fibrils gelated organic solvents by forming 3D entangled networks. The m-substitution feature of the benzene subunits was expected to enable the stacking of the benzene subunits from different molecules because it allowed for the orientation of the conjugated backbones in different directions. Thus, to some extent, the conjugated backbones resemble the aliphatic chains of many reported organogelators in forming 3D networks through van der Waals force,^{1,2} whereas the pyrene subunits allowed for the formation of the 1D aggregates due to a strong face-to-face stacking tendency.



Fig. 3 (a) Emission spectra of 2c in cyclohexane with increasing concentration from 1.0 μM to 1.0 mM. (b) Emission spectra of 2c in solution (0.02 mM) and in the gel state (5.0 mM) in cyclohexane.



Fig. 4 Schematic representation of the hierarchical self-assembly of pyrene-appended oligo(*m*-phenylene ethynylene)s into 3D networks for gelating organic solvents.

The SEM and TEM images of the dried gels of achiral 2c in cyclohexane exhibited fibres with a statistically dominant left-handed (M) or right-handed (P) twist. Although we could not control the M or P twist for a specific sample, all the investigated samples formed an M- or a P-dominant twist in a random manner. The average width of the twists was *ca.* 21 nm.



Fig. 5 CD spectra of **2c** gels (red line, gel suspension) and **2c** solutions (black line, 8.6×10^{-3} M, $60 \,^{\circ}$ C) in cyclohexane and SEM images of the corresponding gels. (a) The M twists outnumber the P twists. (b) The P twists outnumber the M twists.

We further performed circular dichroism (CD) measurements for the gel samples in cyclohexane. It was found that, when the M twists outnumbered the P twists, the corresponding CD spectrum featured a positive Cotton effect around 404 nm and a negative Cotton effect around 434 nm (Fig. 5a), and when the P twists outnumbered the M twists, the CD spectrum showed two opposite Cotton effects of rough mirror-symmetry (Fig. 5b). Heating these cyclohexane gels to 60 $^\circ\mathrm{C}$ led to a gel-to-sol transition, which was accompanied by the disappearance of the CD signals. This uneven symmetry breaking might be similar to that revealed for achiral C3-symmetric molecules and racemic alanine derivatives by Liu and co-workers.¹³ In the early stage of nucleation-elongation, some of the conjugated molecules assembled into 1D helical aggregates, by chance, with a predominant P or M conformation through the π - π stacking of the pyrene subunits. The certain handedness of these helical aggregates then served as a steering wheel to guide other molecules to assemble into the same chiral conformation, probably due to the steric hindrance arising from the overcrowded molecular packing. The hierarchical self-assembly of these small helical aggregates further produced larger twists of the P or M conformation.

In summary, we have reported the first example of conjugated hydrocarbon LMOGs that bear no polar groups, heteroatoms, or alkyl or steroidal moieties. We demonstrate that the large pyrene subunit plays a crucial role in forming 1D stacking aggregates, which further assemble into fibrous structures and then 3D networks. All the hierarchical assembling processes are promoted by the connected oligo(*m*-phenylene ethynylene) chain through stacking of the incorporated benzene subunits. The result opens a new possibility for designing conjugated optoelectronic soft materials. For this purpose, we will further investigate the possibilities of replacing the pyrene subunit with other large aromatic moieties and replacing the ethynylene linkers with vinylene subunits.

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