Oligo(*p*-phenylene-ethynylene)-Derived Super-π-Gelators with Tunable Emission and Self-Assembled Polymorphic Structures

Anesh Gopal,^[a] Reji Varghese,^[a, b] and Ayyappanpillai Ajayaghosh^{*[a]}

Abstract: Linear π -conjugated oligomers are known to form organogels through noncovalent interactions. Herein, we report the effect of π -repeat units on the gelation and morphological properties of three different oligo(*p*-phenylene-ethynylene)s:

OPE3, **OPE5**, and **OPE7**. All of these molecules form fluorescent gels in non-polar solvents at low critical gel concentrations, thereby resulting in a blue gel for **OPE3**, a green gel for **OPE5**, and a greenish yellow gel for **OPE7**. The molecule–molecule and molecule–

substrate interactions in these OPEs are strongly influenced by the conjugation length of the molecules. Silicon wafer suppresses substrate-molecule interactions whereas a mica surface facilitates such interactions. At lower concentrations, **OPE3** formed vesicular assemblies and **OPE5** gave entangled fibers, whereas **OPE7** resulted in spiral

Keywords: conjugation • fluorescence • gels • polymorphism • selfassembly assemblies on a mica surface. At higher concentrations, **OPE3** and **OPE5** resulted in super-bundles of fibers and flowerlike short-fiber agglomerates when different conditions were applied. The number of polymorphic structures increases on increasing the conjugation length, as seen in the case of **OPE7** with n=5, which resulted in a variety of exotic structures, the formation of which could be controlled by varying the substrate, concentration, and humidity.

Introduction

Oligo(*p*-phenylene-ethynylene)s (OPEs) are an important class of π -systems in view of their fluorescence and electronic properties and are potential candidates in molecular and supramolecular electronics.^[1,2] For application in electronic devices, the size- and shape-controlled self-assembly of π -systems are of great importance.^[3] Organogelation is a suitable approach for the creation of nano- to microsized π -systems.^[4] The gelation of poly(*p*-phenylene-ethynylene)s, OPEs, and related systems is known;^[5–7] however, there is no systematic understanding of the effect of the length of π -conjugation (or repeat units) on their self-assembly, gelation, and morphology. Herein, we report how the number of oligomeric repeat units and the associated π -length in the OPEs (**OPE3, OPE5,** and **OPE7**) control the gelation and morphology of the structures through the interplay of sub-

[a] A. Gopal, Dr. R. Varghese, Prof. A. Ajayaghosh Photosciences and Photonics Group Chemical Sciences and Technology Division National institute for Interdisciplinary Science and Technology (NIIST) CSIR, Thiruvanthapuram-695019 (India) Fax: (+91)0471-2491712, 249018 E-mail: ajayaghosh62@gmail.com
[b] Dr. R. Varghese

[0] DI. K. Vagnese Current affiliation: Indian Institute of Science Education and Research, (IISER-TVM) Thiruvanthapuram (India)

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strate-molecule and molecule-molecule interactions. In this way, it is possible to access a variety of polymorphic architectures, such as vesicles, fibers, flowers, spirals, elongated sheets, and entangled super-bundles, as shown in Figure 1.

Fluorescent π -gels that are based on linear π -systems are attracting ever-more attention owing to their potential applications in imaging and sensing.^[8] Previously, we have reported the self-assembly of an OPE that contained three aromatic rings (**OPE3**) into vesicular assemblies,^[6a] thereby



Figure 1. Schematic representation of the polymorphic structures that were derived from the OPEs by subtly controlling the molecular interactions.

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leading to weak gels that were surprisingly different to those from an analogous oligo(p-phenylenevinylene) (OPV), which formed supramolecular tapes and strong gels.^[9] The reason for the vesicle formation of **OPE3** was ascribed to the weak π -interactions in this molecule. Therefore, we anticipated that increasing the conjugation length by varying the number of repeat units in the oligomeric backbone may strongly influence the self-assembly process, thereby leading to the formation of structures with diverse morphologies. With this notion in mind, we prepared molecules **OPE5** (which contains five aromatic rings) and **OPE7** (which contains seven aromatic rings). A detailed investigation of these molecules revealed distinct differences in their self-assembly, gelation, and morphological properties.

Results and Discussion

Molecules OPE3, OPE5, and OPE7 were synthesized by using Sonogashira-Hagihara cross-coupling reactions^[10] as the key step and were characterized by using ¹H and ¹³C NMR spectroscopy and by mass spectrometry (MALDI-TOF MS). The UV/Vis absorption and emission spectra of **OPE3, OPE5**, and **OPE7** ($c = 1 \times 10^{-5}$ M) in CHCl₃ and *n*decane at 25 °C showed the expected effect of conjugation length, with a gradual red-shift in the absorption and emission maxima (Figure 2). In *n*-decane, these compounds exist as aggregates, as evidenced from the red-shifted shoulder bands in the absorption spectra, which were temperature sensitive (see the Supporting Information, Figure S1). Aggregates of **OPE3** and **OPE5** in *n*-decane $(c=1 \times 10^{-5} \text{ M})$ exhibited emission maxima at 445 nm and 506 nm when excited at 419 nm and 464 nm, respectively (Figure 2c). Their corresponding fluorescence quantum yields ($\Phi_{\rm f}$) were 0.54 and 0.42(±0.01) at 25°C (Rhodamine 101 and 6G were used as the standards, respectively).^[11] The emission maximum of OPE7 aggregates occurred at 546 nm (red-shift by almost 100 nm relative to OPE3) when excited at 483 nm, with $\Phi_{\rm f} = 0.31(\pm 0.01)$ at 25 °C (Rhodamine 6G was used as a standard). The aggregates of OPE3 and OPE5 exhibited melting-transition temperatures of 35°C (monitored at 410 nm) and 45°C (monitored at 465 nm), respectively, whereas the aggregate of OPE7 exhibited a melting-transition temperature of 52°C (monitored at 485 nm), thus indicating higher thermal stability for the aggre-



Table 1. Physical properties of oligomers OPE3, OPE5, and OPE7.

a) 1.0 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0	b) 1.0 OPE3 OPE5 OPE7 α 0.5 0.0 30 45 $607/^{\circ}C$
c) 1.0 0.5 Norm 0.0 500 600 700 800 2/nm	d) 60 T_{g}/PC 40 2 4 6 8 10 12 $c/mg mL^{-1}$
e)	f)

Figure 2. a) Absorption spectra of solutions of the OPEs in *n*-decane ($c = 1 \times 10^{-5}$ M) and b) their corresponding melting curves, plotted as the aggregated fractions (*a*) versus temperature (normalized data points were taken from the temperature-dependent UV/Vis absorption spectra). c) Emission spectra of the OPEs in *n*-decane gel (at the minimum gelator concentration). d) Plots of the gel-melting temperature versus the concentration of the gelators. Photographs of the *n*-decane gels under normal light (e) and under UV light (f).

OPE1

OPE2

OPE3

tor concentration (CGC) of 4.5 mgmL⁻¹ (0.6 wt.%) that showed a T_{gel} value of 35 °C, whereas **OPE5** afforded a greenish fluorescent (λ_{em} =540 nm) gel at a CGC of 3.3 mgmL⁻¹ (0.45 wt.%) with T_{gel} =55 °C. Remarkably, **OPE7** could gelate in *n*-decane (greenish-yellow fluorescence) at a CGC of 2.5 mgmL⁻¹ (0.34 wt.%). The corresponding T_{gel} value was 60 °C, which was 25 °C higher than that of **OPE3**. From these data, it is clear that **OPE3**, **OPE5**, and **OPE7** belong to the class of super-gelators.^[12] The gelation data and photophysical properties of these compounds are shown in Table 1.

Transmission electron microscopy (TEM) images of **OPE3**, **OPE5**, and **OPE7** from aged solutions in *n*-decane

		U					
Oligomer	CGC [mgmL ⁻¹]	CGC [wt.%]	$T_{\rm gel}$ [°C]	Absorption λ_{max} [nm]	Emission λ_{max} [nm]	Fluorescence life- time [ns]	$\Phi_{ m f}$ [%]
OPE3	4.5	0.6	35	383, 420	445, 462 ^[a]	$ \tau_1 = 0.70^{[d]} \tau_2 = 5.33 \tau_2 = 1.73 $	54 ^[a]
OPE5	3.3	0.45	55	425, 465	506, 533 ^[b]	$\tau_1 = 0.49^{[e]}$ $\tau_2 = 3.90$ $\tau_2 = 1.11$	42 ^[b]
OPE7	2.5	0.34	60	438, 484	546, 586 ^[c]	$ au_1 = 0.44^{[e]}$ $ au_2 = 4.72$ $ au_3 = 1.12$	31 ^[c]

OPE1

OPE2

[a] Excited at 419 nm; [b] excited at 464 nm; [c] excited at 483 nm; [d] excited at 401 nm; [e] excited at 440 nm.

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Figure 3. TEM morphologies of a) **OPE3** (see reference [7]), b) **OPE5**, and c) **OPE7**, which were obtained from solutions of the OPEs in *n*-decane that were drop-cast onto carbon-coated copper grids at room temperature ($c=1 \times 10^{-5}$ M). The TEM images were obtained without staining.

(after 4 h at 25 °C, $c=1 \times 10^{-5}$ M) are shown in Figure 3. Whilst **OPE3** formed vesicular assemblies (Figure 3 a), **OPE5** resulted in short fibers (Figure 3 b) with an average width of approximately 50 nm and lengths of typically a few micrometers. TEM images of **OPE7** obtained under the same experimental conditions revealed the formation of relatively long fibers of several micrometers in length that had an average width of 30 nm (Figure 3 c). These data indicated that, in dilute solutions, **OPE3** did not result in extended self-assembly, whereas **OPE5** and **OPE7** were capable of forming elongated fibers. In view of this observation, we decided to monitor how these molecules self-assembled on different substrates and at different concentrations under ambient conditions.

Atomic force microscopy (AFM) images of **OPE5** (1×10^{-5} M in *n*-decane,) on silicon wafer and on freshly cleaved mica are shown in Figure 4a and Figure 4b, respectively. On silicon wafer, nanoparticles were present, whereas, interestingly, on the mica surface, entangled fibers were formed. Detailed section analysis revealed that the width of these micrometer-length fibers varied from 60–300 nm with significant height variations of 3.4–13.6 nm (Figure 4c). The AFM images of **OPE7** (1×10^{-5} M in *n*-decane) on silicon surfaces exhibited both particles and fiber morphologies (Figure 4d). Interestingly, on a freshly cleaved mica surface, **OPE7** ex-



Figure 4. AFM images of **OPE5** (*n*-decane, $c = 1 \times 10^{-5}$ M) on silicon wafer (a) and mica surfaces (b) and **OPE7** on silicon wafer (d) and mica surfaces (e). c, f) Zoomed-in images of **OPE5** and **OPE7** with their corresponding cross-section analysis.

hibited a spiral morphology (Figure 4e).^[13] Such substratedependent self-assembly has already been reported in the case of OPVs and other similar systems.^[14] The spiral self-assembly of π -systems is rare and interesting; it indicates an epitaxy-driven process that is associated with the strong interactions between OPE7 and the mica surface. Freshly cleaved mica surfaces are known to facilitate the epitaxial self-assembly of electron-rich molecules, such as tetrathiafulvalenes and thiophenes.^[15] The individual ribbons of the spirals had an average width of approximately 60 nm and lengths of a few micrometers. Surprisingly, a constant height of about 3.4-4.1 nm was observed for the spirals (Figure 4 f). Detailed analysis of different regions of the images clearly showed a uniform height over a broad area (see the Supporting Information, Figure S3), which is unusual for self-assembled π -systems. Thus, **OPE7** exhibits a relatively moredisciplined self-assembly on a mica surface when compared to that of OPE5.

In the case of **OPE5**, the observed heights (3.4, 6.8, 10.2, and 13.6 nm) matched the heights of the mono-, bis-, tris-, and quadruple layers of the self-assembly. Such an arrangement had earlier been proposed by Rabe and co-workers for poly(p-phenylene-ethynylene)s (PPEs) based on AFM analysis.^[16] However, in the case of **OPE7**, the substratemolecule interactions and the molecule-molecule π -interactions overcome the weak van der Waals interactions, thereby suppressing the multilayer lamellar assembly and resulting in nanospirals of uniform height. To confirm the role of freshly cleaved mica in the self-assembly process, we performed AFM analysis of samples that were prepared on an aged mica surface.^[17] Interestingly, spiral formation is not observed in this case (see the Supporting Information, Figure S4). On silicon wafer, OPE5 and OPE7 tend to minimize the surface interactions, thereby resulting in particles. However, on freshly cleaved mica surfaces, substrate-molecule interactions may also become strengthened along with the molecule-molecule interactions. In the case of OPE7, strong substrate-molecule interactions lead to the formation of nanospirals of uniform height. These interactions become predominant during the direct drop-casting of dilute solution of the gelator followed by slow evaporation.

The influence of substrate–molecule interactions can be minimized by performing the self-assembly process in solutions at higher concentrations of the gelator with a subsequent transfer of the self-assembled structures onto the substrate. For this purpose, we allowed the self-assembly of **OPE7** in *n*-decane ($c=1 \times 10^{-5}$ M) by aging the solution for 4 hours and then transferring it onto silicon- and mica surfaces. AFM analysis of these specimens showed elongated fibers in both cases (Figure 5), the morphologies of which were significantly different from those that were obtained by direct solution-casting of the dilute solutions. These experiments strongly suggest that the morphology that is formed by the direct drop-casting of π -systems onto different substrates from dilute solutions may be significantly different to the actual morphology and that any interpretation

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Figure 5. AFM image of **OPE7** from aged solutions in *n*-decane ($c=1 \times 10^{-4}$ M) on silicon wafer (a) and mica surfaces (b). The samples were prepared by drop-casting aged solutions (after 4 h at room temperature) on their respective freshly prepared surfaces.

of the electronic properties of the materials based on such morphological features must be treated with caution.

Because distinct morphological variation was observed by TEM and AFM analysis at lower concentrations in the solution state and on different substrates, respectively, we were keen to identify the morphologies of the structures at higher concentrations and in the gel state. Therefore, we performed scanning electron microscopy (SEM) analysis under different conditions, which resulted in interesting morphological variation. For example, the drop-casting of hot solutions of **OPE3** under dry conditions (<30% humidity, from a 4.5 mg mL⁻¹ solution) resulted in micrometer-sized spherical agglomeration of curved short fibers (Figure 6a). Dropcasting of hot solutions of **OPE5** (3.3 mg mL⁻¹ in *n*-decane) and **OPE7** (2.5 mg mL⁻¹ in *n*-decane) on silicon wafer resulted in the formation of spherical assemblies that were formed from thin flower petal-like structures (Figure 6b, c). The fine features of these spherical structures were observed

from magnified images (Figure 6, insets). From these images, it is also clear that, when a hot solution is drop cast, spontaneous self-assembly occurs under the influence of the substrates. From the AFM and SEM analyses it is clear that OPEs do not interact with the silicon surface and, hence, minimize the molecule-substrate interactions, thus resulting in spherical agglomerates of the short fibers or petals. Interestingly, SEM analysis performed after the molecules are allowed to form gels in the appropriate solvents under sonication, followed by the transfer of the assemblies on silicon substrates, showed entangled supramolecular tapes of several micrometers in length (Figure 6 d-f), which is typical of a gel morphology. This observation indicates that, in this case, the substrate has no role in controlling the morphology. When the same solutions are kept for longer amounts of time, stable gels are formed, the SEM images of which revealed the presence of super-fibers. Careful observation of these fibers indicates that they are formed from wrinkled 2D sheets (Figure 6d–f, insets).

An interesting feature of the self-assembly of **OPE7** is the formation of "ambient-adaptable" polymorphic structures. For example, when a hot solution of **OPE7** (2.5 mgmL⁻¹) is allowed to undergo fast evaporation of the solvent in less than 30% humidity on a silicon surface, flowerlike structures are observed (Figure 7a). However, when a hot solution is evaporated at an extremely slow rate in less than 30% humidity, followed by keeping for 3 days, elongated multi-layered sheets are obtained (Figure 7b). Interestingly, when the hot solution is evaporated at a fast rate at above 80% humidity, micron-sized fused spherical particles are formed (Figure 7c). On the other hand, upon slow evaporation of the same solution in above 80% humidity, wrinkled 2D sheets in the shape of flowers that contain micron-sized cavities are formed (Figure 7d). Such polymorphic self-as-



semblies allow the access of a variety of aesthetic supramolecular architectures of OPE7. In the cases of OPE3 and OPE5, such diverse structures with clear morphological differences could not be observed. Therefore, it is obvious that the strong molecule-molecule and molecule-substrate interactions that are associated with the electron-rich π -repeat units of OPE7 play an important role in the polymorphic self-assembly process. Previous reports on the formation of such polymorphic self-assembly processes strongly support our findings.^[18]

Figure 6. SEM images of the self-assembled OPEs (at the CGC) on silicon-wafer surfaces under different experimental conditions: a-c) The images were obtained when hot solutions of **OPE3**, **OPE5**, and **OPE7**, respectively, were drop-cast under dry conditions (<30% humidity). d-f) Images of the **OPE3**, **OPE5**, and **OPE7** gels, respectively, which were obtained after cooling to room temperature under normal atmospheric conditions and sonication. Insets show images of the same gels after 2 days.

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Figure 7. SEM images of **OPE7** (2.5 mgmL⁻¹ in *n*-decane) on a silicon wafer under different experimental conditions: a,b) The images were obtained under dry conditions (<30% humidity) with fast and slow evaporation of the solvents, respectively. c,d) The images were obtained under wet conditions (>80% humidity) with fast and slow evaporation of the solvents, respectively.

Conclusions

In conclusion, we have revealed the influence of the length of the oligomer in a linear π -system on molecule–molecule

and molecule-substrate interactions, which, in turn, influence the morphological features of the structure. As the conjugation length is increased, the stability of the aggregates and the gels increases with a significant red-shift in the emission. More importantly, this study provides an insight into the surface and "ambient-adaptable" self-assembly of extended π -systems, thereby allowing access to a variety of aesthetically appealing super-structures. At this point, the challenge to the scientific community is how to precisely engineer a certain structure of an organic semiconductor out of the available polymorphic structures to, in principle, be able to achieve a desired electronic property for a required application.

Experimental Section

Materials

All starting materials and reagents were purchased from commercial suppliers and used without further purification. The solvents were purified and dried by using standard methods prior to use.

Synthesis and Characterization

The OPEs were synthesized through step-by-step Sonogashira–Hagihara Pd-catalyzed cross-coupling reactions. The synthetic route is described in Scheme 1. 1,4-Bis(dodecyloxy)2,5-diethynylbenzene(1),^[6a] 2,5-bis(dodecyloxy)-4-iodobenzaldehyde (2),^[21] ((2,5-bis(dodecyloxy)-4-iodophenyl) ethynyl)trimethylsilane (3),^[20] and **OPE3**^[6a] were synthesized according to literature procedures.

5,5'-(2,5-Bis(dodecyloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)bis(1,4-bis(dodecyloxy)-2-ethynylbenzene) (4)

Compound 1 (0.34 mmol), ((2,5-bis(dodecyloxy)-4-iodophenyl)ethynyl)trimethylsilane (3, 0.75 mmol), CuI (0.034 mmol), and [Pd(PPh₃)₂Cl₂] (0.034 mmol) were dissolved in THF/diisopropylamine (20 mL, 1:1), and the mixture was stirred under an argon atmosphere at RT for 24 h. The mixture was poured into MeOH (50 mL) and the formed precipitate was filtered. The yellow precipitate was dissolved in a THF/MeOH mixture (20 mL, 1:1) followed by the addition of excess K₂CO₃ and the reaction mixture was stirred for 24 h. After removal of the solvent under reduced pressure, the bis-ethynylene compound (4) was separated by column chromatography on silica gel (n-hexane/CHCl₃, 3:1). Yield: 60%; m.p. 91–93 °C; ¹H NMR (300 MHz, CDCl₃): $\delta = 6.92$ (s, 2 H), 6.91 (s, 2 H), 6.90 (s, 2H), 3.93 (t, 12H), 3.26 (s, 2H), 1.76-1.74 (m, 12H), 1.49-1.43 (m, 24H), 1.17 (m, 84H), 0.81 ppm (t, 18H); ¹³C NMR (125 MHz, CDCl₃, TMS): $\delta = 14.23$, 22.32, 25.16, 29.02, 29.05, 31.19, 69.46, 79.28, 82.82, 91.74, 112.23, 118.11, 146.05, 153.05 ppm; MS (MALDI-TOF): m/z calcd for C₁₆₂H₂₆₂O₁₀: 1433.3 [*M*+H]⁺; found: 1433.1.



Scheme 1. Synthesis of the OPEs. Reagents and conditions: a) $[Pd(PPh_3)_2Cl_2]$ (5 mol %), CuI (5 mol %), diisopropylamine/THF (1:1 v/v), 30 °C, 24 h; b) NaBH₄, MeOH/CH₂Cl₂ (1:2 v/v), 30 °C, 2 h; c) K₂CO₃, THF/MeOH (2:1 v/v), 30 °C, 6 h.

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5,5'-(2,5-Bis(dodecyloxy)-1,4-phenylene) bis(ethyne-2,1-diyl)bis(2-((2,5-bis (dode-cyloxy)-4-ethynylphenyl)ethynyl)-1,4-bis(dodecyloxy)benzene) (5)

A mixture of compound 4 (0.167 mmol), ((2,5-bis(dodecyloxy)-4-iodophenyl)ethynyl)trimethylsilane (3) (0.368 mmol), CuI (0.032 mmol), and [Pd(PPh₃)₂Cl₂] (0.017 mmol) in diisopropylamine (10 mL) and THF (10 mL) was stirred for 24 h at RT under an argon atmosphere. The reaction mixture was then precipitated with MeOH. The yellow precipitate was dissolved in a THF/MeOH mixture (20 mL, 1:1), excess K₂CO₃ was added, and the mixture was stirred for 24 h. After removal of the solvent under reduced pressure, the bis-ethynylene compound that was formed (5) was purified by column chromatography on silica gel (n-hexane/ CHCl₃, 3:1). Yield 20%; m.p. 103–105°C; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.00$ (s, 2 H), 6.98 (s, 2 H), 6.97 (s, 6 H), 4.02–4.0 (t, 20 H), 3.33 (s, 2 H), 1.83 (m, 20H), 1.55-1.50 (m, 30H), 1.24 (m, 150H), 0.86 ppm (t, 30H); ¹³C NMR (125 MHz, CDCl₃, TMS): $\delta = 15.12$, 21.62, 25.65, 29.01, 29.95, 30.25, 30.65, 30.88, 31.69, 60.56, 67.88, 90.74, 111.78, 112.03, 120.98, 122.36, 127.78, 150.05, 156.69 ppm; MS (MALDI-TOF): m/z calcd for $C_{162}H_{262}O_{10}$: 2370.81 [*M*+H]⁺; found: 2370.12.

OPE5

Compound 4 (50 mg, 0.035 mmol), 4-iodo-2,5-bis(dodecyloxy)benzaldehyde (0.08 mmol) (2), $[Pd(PPh_3)_2Cl_2]$ (10 mol%), and CuI (10 mol%) were dissolved in a degassed mixture of diisopropylamine (10 mL) and THF (10 mL). The mixture was stirred under an argon atmosphere at 40°C for 24 h. After cooling to RT, the mixture was added dropwise to vigorously stirring MeOH. The pale-yellow solid of bis-aldehyde (30 mg) that was obtained was dried and redissolved in a mixture of MeOH (10 mL) and CH₂Cl₂ (20 mL) and was reduced into its corresponding alcohol with NaBH₄ (4 equiv) at RT. The mixture was washed with water and extracted with CH2Cl2. The product was precipitated with MeOH. The crude product was further purified by column chromatography on silica gel (n-hexane/CHCl₃, 1:1). Yield: 60%; m.p. 140-143°C; ¹H NMR (300 MHz, CDCl₃, TMS): δ=6.93 (s, 2H), 6.93 (s, 6H), 6.82 (s, 2H), 4.61 (s, 4H), 3.97-3.88 (t, 20H), 2.25 (t, 2H,), 1.77(m, 20H), 1.48 (m, 30H), 1.17 (m, 150H), 0.81-0.79 ppm (t, 30H); ¹³C NMR (125 MHz, CDCl₃, TMS): $\delta = 14.93$, 22.52, 25.25, 29.01, 29.95, 30.18, 31.69, 60.56, 67.88, 68.74, 84.34, 111.28, 112.03, 118.18, 122.36, 134.78, 146.05, 155.88 ppm; MS (MALDI-TOF): *m*/*z* calcd for C₁₆₀H₂₆₆O₁₂: 2382.82 [*M*+H]⁺; found: 2382.42.

OPE7

OPE7 was prepared by a coupling reaction between diethynylene compound **5** (0.021 mmol) and 4-iodo-2,5-bis(dodecyloxy)benzaldehyde (**2**, 0.084 mmol) under the same experimental conditions as for **OPE5**. The crude product was further purified by column chromatography on silica gel (*n*-hexane/CHCl₃, 3:1). Yield: 55%; m.p. 150–153°C; ¹H NMR (300 MHz, CDCl₃): δ = 7.01 (s, 2H), 7.00 (s, 2H), 6.99 (s, 10H), 4.68 (s, 4H); 4.02–4.0 (t, 28H), 2.17 (s, 2H), 1.83 (m, 28H), 1.55–1.50 (m, 56H), 1.24 (m, 196H), 0.86 ppm (t, 42H); ¹³C NMR (125 MHz, CDCl3, TMS): δ = 14.90, 22.62, 24.54, 25.65, 29.01, 29.85, 30.01, 30.65, 30.98, 32.52, 60.06, 65.06, 67.88, 70.01, 70.67, 79.74, 95.28, 112.03, 120.98, 130.36, 145.78, 150.05, 156.69 ppm; MS (MALDI-TOF): *m/z* calcd for C₂₂₄H₃₇₀O₁₆: 3320.33 [*M*+H]⁺; found: 3319.80.

Instruments and Measurements

¹H and ¹³C NMR spectra were measured on 300 MHz and 500 MHz Bruker Avance DPX spectrometers with TMS as an internal standard. Matrix-assisted laser-desorption ionization time-of-flight (MALDI-TOF) MS was performed on an AXIMA-CFR PLUS (SHIMADZU) MALDI-TOF mass spectrometer. High-resolution MS was performed on a JEOL JM AX 505 HA mass spectrometer. Melting points were determined with an MEL-Temp-II melting-point apparatus and are uncorrected. Electronic absorption spectra were recorded on a Shimadzu UV-3101 PC NIR scanning spectrophotometer and the emission spectra were recorded on a SPEX-Flourolog F112X Spectrofluorimeter. Variable-temperature studies were carried out in a 1 cm quartz cuvette with a thermistor that was directly attached to the wall of the cuvette holder. The fluorescence quantum yield was calculated according to a literature procedure^[11] by using Rhodamine 6G (in EtOH, $\Phi_f=0.94$ at 22°C) and Rhodamine 101 (in EtOH, $\Phi_f=1$ at 25°C) as standards.^[22] Atomic force microscopy (AFM) images were recorded under ambient conditions by using a Digital Instrument Multimode Nanoscope IV operated in the tapping-mode regime. Microfabricated silicon cantilever tips (MPP-11100–10) with a resonance frequency of 299 kHz and a spring constant of 20–80 Nm⁻¹ were used. The scan rate was varied from 0.5 to 1.5 Hz. To rule out the possibility of any artifacts, we carried out blank experiments after evaporation of the neat solvents on the substrates. AFM section analysis was done offline. TEM was performed on a JEOL-JEM0310 microscope with an accelerating voltage of 80 kV. TEM images were obtained without staining. SEM images were obtained on on a Zeiss EVO 18 cryo Special Edn SEM equipped with a variable-pressure detector working at 20–30 kV. The prepared SEM samples were sputter-coated (Au/Pd) before imaging.

Gel Characterization

The gelation studies were carried out according to literature procedures.^[19] In a typical procedure, a known amount of the required OPE was added to the solvent (1 mL) in a glass vial and the mixture was heated to dissolve the gelator. After cooling to RT, the vessel was turned upside down to verify the gel formation. The reversibility of the gelation process was confirmed by repeated heating and cooling. The critical gelator concentration (CGC) was the minimum amount of the gelator that was required for the formation of a gel at RT (22 °C). The gel-melting temperature (T_{gel}) in *n*-decane was measured by the dropping-ball method.

Sample Preparation for Morphological Analysis

The samples were prepared by solution drop-casting at required concentrations and under different atmospheric conditions. The drying atmosphere was controlled by keeping the sample in a closed desiccator under various pressures and humidity. AFM samples for imaging were prepared on freshly cleaved mica surfaces or pre-cleaned silicon-wafer surfaces. Samples for TEM analysis were prepared on carbon-coated copper grids without staining. Samples for the SEM studies were prepared on a silicon-wafer substrate that was pasted above an aluminum stub by using a conductive carbon tape.

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Self-Assembly

Anesh Gopal, Reji Varghese, Ayyappanpillai Ajayaghosh*______

Oligo(p-phenylene-ethynylene)-Derived Super-π-Gelators with Tunable Emission and Self-Assembled Polymorphic Structures



 π in the sky: The π -conjugated repeat units of oligo(*p*-phenylene-ethynylene)-based super-gelators influenced the molecule–molecule and molecule– substrate interactions in self-assembly processes. Silicon wafer suppressed substrate–molecule interactions whilst mica surfaces facilitated such interactions. The formation of polymorphic structures could be controlled by changing the substrate, concentration, and humidity.

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