

Accepted Article

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To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201704294 Angew. Chem. 10.1002/ange.201704294

Link to VoR: http://dx.doi.org/10.1002/anie.201704294 http://dx.doi.org/10.1002/ange.201704294

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Cooperative Supramolecular Polymerization of Fluorescent Platinum Acetylides for Optical Waveguide Applications

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Abstract: One-dimensional organic structures with well-oriented π -aggregation, strong emission, and ease of processability are desirable for optoelectronic waveguiding devices. Herein, we have developed an unprecedented strategy to attain this objective, by self-assembling platinum(II) acetylides into fluorescent supramolecular polymers *via* cooperative mechanism. The resulting high-molecular-weight supramolecular polymers are capable of forming electrospun microfibers with uniform geometry and smooth surface, which enable light propagation with extremely low scattering loss (0.008 dB μ m⁻¹). With the elaborate combination of bottom-up supramolecular polymerization and top-down electrospinning techniques, this work offers a novel and versatile avenue toward high-performance optical waveguiding materials.

Employing one-dimensional (1D) structures for optical waveguide interconnectors has demonstrated promising prospects for next-generation information and communication technologies.¹ Apart from 1D inorganic materials,² their organic counterparts have gained much attention in recent years. In this respect, m-conjugated polymers and small-molecule-based crystals are regarded as two candidates. For π-conjugated polymers, despite the ease of processability, their inhomogeneous structure and amorphous property hamper the waveguiding performances.³ In contrast, mono-disperse π-smallmolecules have displayed comparatively enhanced and easily tunable functionalities, due to their precisely-defined chemical structure and well-oriented aggregation behaviors.⁴ However, too strong stacking tendency leads to poor processability and difficulty in size/shape control for the resulting crystals.⁵

On this account, it is intriguing to self-assemble π -aromatic small-molecules into processable polymers,⁶ which combine the advantages and avoid the drawbacks for the above two systems. The primary challenge lies in the formation of self-assembled polymers with high degree of polymerization (DP) value. In this regard, natural 1D self-assembled polymers such as tobacco mosaic virus and cytoskeleton proteins provide an inspiration.⁷ They tend to adopt cooperative self-assembly mechanism, consisting of the successive nucleation and elongation steps. By

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employing nucleation step as the self-checking process, highmolecular-weight supramolecular polymeric assemblies are prone to form, whilst unstable oligomers that lack the excellent processability of their polymeric counterparts can be excluded.⁸

In this work, we sought to develop an unprecedented bioinspired strategy toward optical waveguide applications, by selfassembling π -aromatic monomers into supramolecular polymers via cooperative mechanism. It is widely known that, to induce cooperativity for natural 1D self-assembled polymers, multiple non-covalent interactions with more than two nearest neighbors should be embedded in the monomeric structure.7b-c Following this principle, herein platinum acetylide monomer 1 has been designed (Scheme 1). Specifically, two amides are attached on both ends of the platinum(II) acetylide rod, which are capable of forming two-fold intermolecular hydrogen bonds. As a consequence, high-molecular-weight supramolecular polymers are expected to form for 1 via cooperative self-assembly mechanism, which enable the manufacture of 1D fibers via costeffective electro-spinning techniques (Scheme 1).9 Due to the interplay between Pt d-orbitals and p-orbitals of the benzothiadiazole acetylide ligand on 1, the electrospun fibers feature intriguing optical properties, which can be further utilized for light propagation (Scheme 1).¹⁰ Hence, the current study provides a novel and versatile avenue toward waveguiding materials, with the marriage of bottom-up supramolecular polymerization and top-down electro-spinning techniques.

Self-assembly of 1 was firstly investigated by means of solvent-dependent spectroscopic experiments. In chloroform (c = 4 x 10^{-4} M), the maximum UV-Vis absorption bands are located at 350 nm and 482 nm, respectively (Figure 1a). With reference to previous literatures, the former band can be assigned to intra-ligand $\pi-\pi^*$ (IL) transition, while the latter one (dπ(Pt)→π*(C≡Ccharacteristic metal-to-ligand is for benzothiadiazole-C≡C)) charge transfer (MLCT) band.¹¹ When switching solvent from the chloroform to apolar methylcyclohexane (MCH), the maximum MLCT absorption band is bathochromic shifted to 488 nm (Figure 1a). Upon varying the temperature, the presence of two isosbestic points (λ = 398 and 510 nm) illustrates the reversible transition between monomeric and aggregated states (Figure 1b).

In the meantime, the MLCT emission band of 1 locates at 566 nm in MCH (Figure 1a), with the fluorescent lifetime of 4.86 ns. When comparing to that in chloroform (λ_{em} = 595 nm, Figure 1a), it shows 2-fold hyperchromic effect. Switching-on fluorescence in apolar MCH medium should be ascribed to the prevention of carbon–carbon and carbon–platinum bond rotation, leading to the decrease of non-radiative decay upon π -aggregation.¹²

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Scheme 1. Schematic representation for the cooperative supramolecular polymerization of platinum acetylide monomer **1** for optical waveguiding applications.

Circular dichroism (CD) spectroscopy is a powerful technique to probe the regularity of the self-assembled structures, considering that bisignate CD signals only emerge for helical assemblies with long-range order.13 On this account, optically active (S)-3,7-dimethyloctyl groups are introduced to the peripheral side chain of 1 (Scheme 1), which potentially induce helical bias for the resulting aggregates. In chloroform, molecularly dissolved state dominates for 1 ($c = 1 \times 10^{-4}$ M, 278 K), as reflected by the absence of Cotton effect (Figure 1c). In comparison, a moderate bisignate Cotton effect is observed in MCH for the IL transition, with a negative maximum at 364 nm $(\Delta \epsilon = -65.6 \text{ L mol}^{-1} \text{ cm}^{-1}, g = -0.0013)$ and a positive maximum at 351 nm ($\Delta \epsilon$ = 92.8 L mol⁻¹ cm⁻¹, g = 0.00096) (Figure 1c). Additionally, a weak Cotton effect appears in the MLCT region $(\Delta \varepsilon = -17.5 \text{ L mol}^{-1} \text{ cm}^{-1}, g = -0.00074 \text{ for } \lambda = 517 \text{ nm}).^{14} \text{ It}$ unambiguously supports that, in apolar MCH solution, 1 expresses chirality at the supramolecular level, leading to the formation of single-handed polymeric assemblies. For the counterpart monomer 2 with the absence of the amide linkages (Scheme 1), no CD signal can be detected under the same conditions (Figure 1c). Such phenomena highlight the importance of the connective amide units for the formation of long-range-ordered polymeric structures.

Mechanistic insights into the self-assembly process were further performed via temperature-dependent CD spectroscopic measurements (Figure 1d, inset). The bisignated CD signals for 1 are completely lost at elevated temperature and restored upon cooling, suggesting the transition between helical supramolecular polymeric and monomeric states. A slow cooling rate of -0.67 K/min was applied to guarantee thermodynamically controlled supramolecular polymerization of 1 (Figure S23 in the Supporting Information). Notably, a non-sigmoidal cooling curve is obtained by monitoring the CD intensity at 364 nm versus temperature (Figure 1d and Figure S24), supporting the involvement of nucleation-elongation cooperative mechanism.8 The cooling curve is further fitted by the Meijer-Schenning-Vander-Schoot mathematical model (see Eq. S1 and S2 in the Supporting Information).¹⁵ Depending on the non-linear leastsquares analysis (Figure 1d), the T_e (critical elongation temperature) value is determined to be 291 K, while the h_e (enthalpy release upon elongation) value is -93.4 kJ/mol. Additionally, K_a (dimensionless equilibrium constant of the activation step at T_e) value is calculated to be 3.63 × 10⁻⁴, suggesting that a nucleus consisting of 14 molecules is required before activation to the stable chiral stack (Eq. S3). The DP value of **1** is determined to be 242 at 278 K, validating the highmolecular-weight nature for the resulting supramolecular polymers (Eq. S4).



Figure 1. (a) UV-Vis (solid line) and fluorescent (dash line, $\lambda_{ex} = 485$ nm) spectra of 1 ($c = 4 \times 10^{-4}$ M) in MCH (red line) and chloroform (black line). (b) Temperature-dependent UV-Vis spectra of 1 ($c = 4 \times 10^{-4}$ M) in MCH. The arrow shows the transition upon increasing the temperature from 283 K to 318 K. (c) CD spectra of 1 in chloroform (black line), MCH (red line) and 2 in MCH (green line) ($c = 1 \times 10^{-4}$ M, 278 K, 1 mm cuvette). (d) Normalized CD intensity of 1 at 364 nm *versus* temperature (cooling rate: -0.67 K/min). The red and green lines denote the mathematical fitting *via* the Meijer-Schenning-Van-der-Schoot model.¹⁵ Inset: temperature-dependent CD spectra of 1 at every 5 K.

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¹H NMR experiments were further performed to clarify the non-covalent driving forces for supramolecular polymerization process. Monomer 1 shows distinct ¹H NMR signals in dchloroform, whilst severe peak broadening phenomena are observed in d_{12} -cyclohexane (see Figures S26 and S28), denoting the strong aggregation tendency in apolar medium. Upon increasing the monomer concentration from 0.63 mM to 20.0 mM in d-chloroform, the aromatic protons almost remain unchanged, whilst amide resonances shift downfield (0.15 ppm, Figure S27). Such phenomena demonstrate that intermolecular hydrogen bonds, rather than π - π stacking interactions, play a crucial role for supramolecular polymerization. The conclusion is further validated by semi-empirical PM6 calculation. Specifically, for the optimized geometry of the dimeric structure $\mathbf{1}_2$ (Figure 2b), H---O bond lengths between the two neighboring amide groups are determined to be 2.14 Å and 2.09 Å, along with the N-H---O bond angles of 159.7° and 155.8°, respectively. Comparing with the monomeric structure 1 (Figure 2a), the dihedral angles between benzothiadiazole units and P(C₂H₅)₃ ligands exhibit dramatic changes for $\mathbf{1}_2$ (from 22.0° to 34.2° and 45.3°). Accordingly, it suggests that 1 undergoes structural transition from disfavored to preferred conformations during the supramolecular polymerization process.^{10b}



Figure 2. Optimized geometries of (a) monomeric structure 1, and (b) dimeric structure 1_2 , on the basis of semi-empirical PM6 calculations.

Noteworthy, 1 is capable of forming red-color gels in MCH (critical gelation concentration: ~0.01 mol/L at 293 K), which undergo reversible sol-gel transition upon varying the temperature (Figure 3a). Based on rheological experiments (Figure S29), elastic modulus G' and viscous modulus G'' values are independent of the oscillation frequency (frequency range: 0.1–200 rad s⁻¹). Meanwhile, G' (an average value of 5093 Pa) is remarkably higher than G'' (an average value of 1056 Pa) at all tested frequencies. Both G' and G' moduli are almost unchanged within a long time, revealing that the supramolecular gels are sufficiently stable. Depending on transmission electron microscopy (TEM) (Figure 3b) and atomic force microscopy (AFM) (Figure S30) experiments, entangled networks can be visualized for the resulting gels. Hence, supramolecular polymers of 1 tend to bundle with each other, which entrap apolar MCH solvent and thereby form gels in a hierarchical selfassembly manner.

In view of the high-molecular-weight nature of **1** in the selfassembled form, electro-spinning technique was further employed for the fabrication of macroscopic 1D fibers. Specifically, when subjecting a concentrated MCH solution of **1** (0.02 mol/L) to the voltage of 8800 V, microfibers with uniform diameter (4.2 µm) form (Figure 3c). Conversely, droplets instead of fibers were obtained for the counterpart monomer **2** even at higher concentration (Figure 3d). Such phenomena emphasize the superiority of high-molecular-weight supramolecular polymeric structures for the excellent processability. For the electro-spun microfibers derived from **1**, almost no spectral overlap exists between the absorbance (487 nm) and emission (631 nm, see Figure 4c, inset) signals, which is ideal for light propagation and manipulation.^{4d}



Figure 3. (a) Thermo-responsive sol-gel transition of 1 in MCH. (b) TEM image of 1 ($c = 10^{-3}$ M in MCH solution) on a carbon coated copper grid. Bright-field images of (c) 1, and (d) 2 on the glass substrate upon electrospinning technique.

The potential of 1 for optical waveguiding application was further exploited. Briefly, we expanded a 532 nm laser beam (Ar laser, 10 mw) to cover the rear aperture of the objective (60 X,N.A. 1.42), which irradiates the electro-spun microfibers derived from 1. Tip emission signals of 1 are collected by the charge-coupled device camera (Nikon DS-U2) and the spectrometer (iHR550, HORIBA) (Figure 4a). Upon local excitation of the micro-fiber (width: ~4.2 µm, length: ~180 µm), light propagation along the microfibers is visualized via graycolor far-field fluorescent microscopy images (Figure 4b). The out-coupled light intensity decreases exponentially as a function of propagation distance (Figure 4c), which is characteristic for active waveguides.⁴ The propagation loss coefficiency is determined to be 18.9 cm⁻¹ (±10%), corresponding to the propagation loss of 0.008 dB µm⁻¹. Remarkably, such a value is much lower than those of the reported π -conjugated polymeric waveguiding systems (0.13-0.89 dB µm⁻¹).3 We rationalized that well-oriented aggregation and strong emission of the supramolecular polymers, together with the smooth surface of the electro-spun microfibers, facilitate light propagation with dramatically reduced scattering loss.

The preferred direction of chain alignment in the electro-spun microfibers can be further determined *via* polarization-dependent fluorescent measurements (Figure 4d). With the collection polarizer oriented at 30° and 210°, the highest intensities can be observed for the emission peaks centered at 631 nm. On the contrary, it displays the lowest fluorescent intensities at the polarized angles of 120° and 300°. Hence, slip angle between the stacking orientation of **1** and long axis of the electro-spun microfiber is around 30° (Figure 4a). An emission dichroic ratio ($R_d = I_{30°} / I_{120°}$) of 2.5 is obtained, corresponding to the polarization-dependent emission behavior is highly reproducible, whilst *cos*² curves can be fitted very well to these data (Figure 4d). Hence, it indicates excellent waveguiding anisotropy for the fluorescent microfibers.

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Figure 4. (a) Experimental set-up for the optical waveguiding equipment. (b) Top: bright field optical image; bottom: fluorescent images showing optical waveguide of 1 upon laser excitation at different positions. (c) I_{out}/I_{in} *versus* propagation distance and the corresponding mathematical fit (red line). Inset: spatially resolved fluorescence of waveguide emission out-coupled at the tip of the microfiber. (d) Polar image of the peak intensities. The solid curve shows the cos^2 fit.

In summary, herein an unprecedented strategy toward optical waveguiding materials has been developed, by self-assembling fluorescent platinum acetylide monomers into high-molecularsupramolecular polymers via nature-mimicking weight nucleation-elongation mechanism. The combination of "bottomup" supramolecular polymerization and "top-down" electrospinning techniques renders well-oriented m-aggregation and intriguing fluorescence to the microfibers, facilitating optical waveguiding with extremely low scattering loss. Hence, it demonstrates that rational engineering of self-assembly mechanism exerts crucial importance for the development of high-performance optoelectronic materials.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21674106), the Fundamental Research Funds for the Central Universities (WK3450000001), and CAS Youth Innovation Promotion Association (2015365).

Keywords: cooperative effects • molecular recognition • optical waveguide • platinum • supramolecular chemistry

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Platinum acetylides are self-assembled into high-molecular-weight supramolecular polymers *via* nature-mimicking nucleation–elongation mechanism, which enable the cost-effective fabrication of uniform 1D fluorescent microfibers. Such a combination of "bottom-up" self-assembly and "top-down" electro-spinning techniques provides an efficient strategy toward high-performance optical waveguiding materials.

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