

Cooperative Supramolecular Polymerization of Propeller-Shaped Triphenylamine Cyanostilbenes for Explosive Detection

Long-Yu Guang^{a,†}, Zhi-Feng Zhou^{b,†}, Yi-Fei Zhang^a, Lai-Wei Gao^a, Feng Wang^{a*}, and Rui Liao^{a*}

^a CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China

^b Clinical Laboratory, The Second People's Hospital of Hefei, Hefei 230011, China

 Electronic Supplementary Information

Abstract Self-assembly of π -conjugated compounds into supramolecular polymers has received considerable attention because of their intrinsic scientific interests and technological applications. As compared to π -conjugated rods, discotics, and macrocycles, propeller-shaped π -conjugated molecules have been less exploited to form long-range-ordered supramolecular polymers. Herein a novel type of supramolecular polymers has been constructed on the basis of propeller-shaped triphenylamine cyanostilbenes. The designed compound adopts nucleation–elongation cooperative mechanism for the supramolecular polymerization process, because of the participation of three-fold hydrogen bonds between the neighbouring monomers. The supramolecular polymeric state displays amplified chirality and enhanced emission than those in the monomeric state. The resulting supramolecular polymers exhibit severe emission quenching upon addition of 2,6-dinitrotoluene, ascribed to photoinduced electron transfer from the triphenylamine cyanostilbenes to the explosive analyte. The current study proves the feasibility to supramolecularly polymerize propeller-like π -conjugated molecules, serving as a promising type of explosive sensor owing to their guest encapsulation and signal amplification capabilities.

Keywords Supramolecular polymers; D- π -A molecules; Supramolecular chirality; Fluorescence; Explosive detection

Citation: Guang, L. Y.; Zhou, Z. F.; Zhang, Y. F.; Gao, L. W.; Wang, F.; Liao, R. Cooperative supramolecular polymerization of propeller-shaped triphenylamine cyanostilbenes for explosive detection. *Chinese J. Polym. Sci.* 2023, 41, 585–592.

INTRODUCTION

Supramolecular assembly of π -conjugated molecules into ordered nanostructures has received tremendous attentions because of their promising applications in sensing,^[1–5] optoelectronic,^[6–8] and energy conversion fields.^[9,10] Although π -conjugated compounds exhibit the intrinsic stacking capability, they are commonly prone to form ill-defined oligomeric aggregates.^[11–14] It is ascribed to the independent interaction of two π -faces for the π -conjugated molecule, giving rise to the isodesmic supramolecular assembly mechanism.^[15] Accordingly, it is fascinating to develop π -conjugated supramolecular polymers in a long-range-ordered manner, which bring superior properties toward the tailored functionality.^[16,17] To attain this objective, natural supramolecular systems such as actin filaments and tobacco mosaic virus provide some inspiration, involving cooperative

self-assembly mechanism with the successive “nucleation” and “elongation” steps. By employing the “nucleation” step as the self-checking process, these natural supramolecular systems are capable of forming high-molecular weight polymeric nanostructures.

The prerequisite toward cooperative assembly mechanism in natural supramolecular systems is to incorporate multiple non-covalent interactions per monomeric unit with more than two nearest neighbours. Taking it as an inspiration, a key design principle in artificial supramolecular systems is to attach amides (or ureas) neighbouring to the π -conjugated unit.^[18,19] It facilitates non-covalent complexation of the π -conjugated monomers *via* multivalent π - π stacking and hydrogen bonding interactions, and thereby induces cooperativity for the supramolecular assembly process. Although a variety of cooperative supramolecular π -conjugated polymers have been constructed with the aid of hydrogen bonds, they are primarily limited to rod-like,^[20] discotic-like,^[21,22] and macrocyclic-like π -conjugated molecules with the planar geometry.^[23,24] In comparison, cooperative supramolecular polymerization of propeller-shaped π -conjugated molecules have been far-less exploited. Triphenylamines represent a typical type of propeller-shaped π -conjugated molecules, with multiple rigid arms in a non-planar manner. The resulting supra-

* Corresponding authors, E-mail: drfwang@ustc.edu.cn (F.W.)
E-mail: rliao@ustc.edu.cn (R.L.)

[†] These authors contributed equally to this work.

Special Issue: The Youth Innovation Promotion Association of the Chinese Academy of Sciences

Received October 21, 2022; Accepted December 1, 2022; Published online January 16, 2023

molecular nanostructures could potentially display unique properties due to the steric congestion effect.^[25] On this account, it is intriguing to assemble triphenylamine and their derivatives into long-range-ordered supramolecular polymers.

Herein, we sought to develop cooperative supramolecular polymers by employing triphenylamine cyanostilbenes as the propeller-shaped core. For the designed monomer (*R*)-**1** (Scheme 1), three *N*-[(1*S*)-phenylethyl]-benzamides were embedded to induce cooperativity *via* the participation of three-fold hydrogen bonds. The wedge-shaped alkyl chains in the peripheries provide sufficient solubility, capable of forming supramolecular polymers in apolar media. In terms of the propeller-shaped π -conjugated core, triphenylamine and thiophene units serve as the electron-pushing donors (D), while the three cyanostilbene arms act as the electron-withdrawing acceptors (A). The D- π -A unit features aggregation-induced emission character, endowing the resulting supramolecular polymers with strong emission intensity. In addition, the propeller-shaped D- π -A core exhibits excellent encapsulation capability toward the guest, namely 2,6-dinitrotoluene (2,6-DNT). Electron transfer occurs between (*R*)-**1** and 2,6-DNT due to energy matching between their lowest unoccupied molecular orbitals (LUMOs). The long-range-ordered supramolecular polymers bring signal amplification effects, leading to severe emission quenching upon adding 2,6-DNT to (*R*)-**1** (Scheme 1). Since 2,6-DNT is analogue to trinitrotoluene (TNT) with commercial unavailability, the current supramolecular polymeric system can be regarded as a candidate to achieve fluorescence-based explosive detection.

EXPERIMENTAL

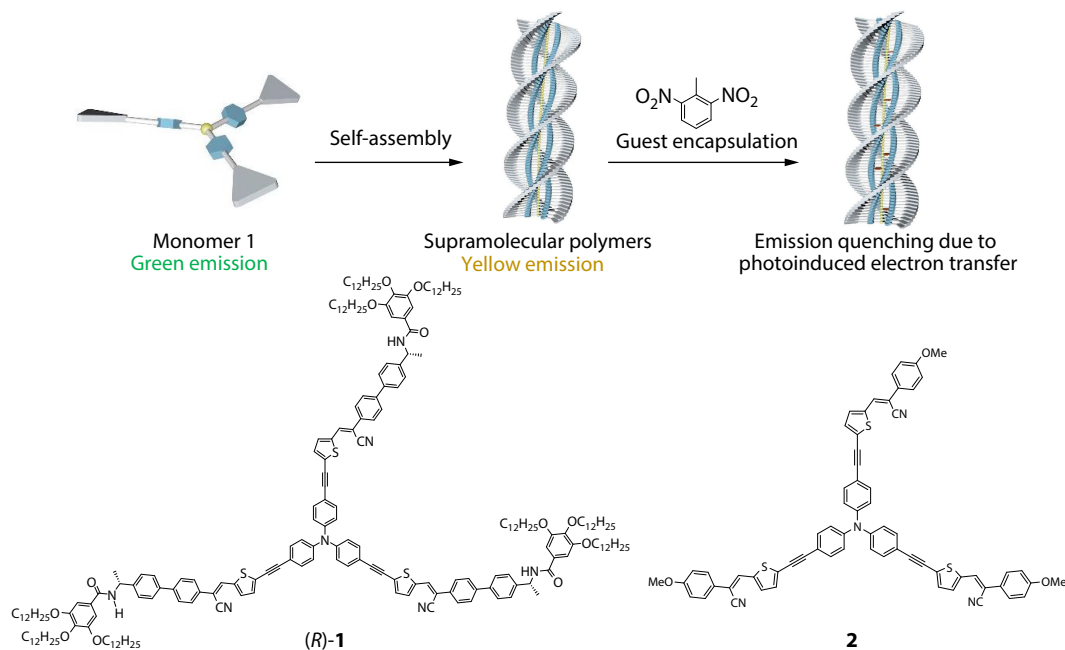
General Considerations

All moisture/oxygen sensitive reactions were performed using

Schlenk techniques under N₂. Potassium *tert*-butoxide, *tert*-butanol, (*R*)-4-bromo- α -methylbenzylamine, tri(4-iodophenyl)amine, 4-methoxyphenylacetonitrile, and 5-bromo-2-thiophenecarboxaldehyde were reagent grade and used as received. The intermediate compounds **3–6** (Scheme S1 in the electronic supplementary information, ESI) were synthesized according to the previous studies. Other reagents and solvents were employed as purchased. ¹H- and ¹³C-NMR spectra were recorded on a Bruker DMX-400 (400 MHz for ¹H, 101 MHz for ¹³C) instrument. MALDI-TOF measurements were recorded on a Bruker Autoflex Speed spectrometer with DCTB as the matrix. UV-Vis spectra were recorded on a UV-1800 Shimadzu spectrometer. Circular dichroism (CD) measurements were performed on a Jasco J-1500 circular dichroism spectrometer, equipped with a PFD-425S/15 Peltier-type temperature controller. Photoluminescence spectra were recorded using Hitachi F4600. AFM measurements (tapping mode) were performed using a Bruker Dimension Icon with ScanAsyst system in air with silica cantilevers (RFESPA-75, Ohm-cm Antimony (n) doped Si) and a resonance frequency of ~75 kHz and a spring constant of ~3 N·m⁻¹. The images were analysed using the Pico Image processing program.

DFT Theoretical Calculations

Optimization of the structures were performed using the semiempirical PM7 method as implemented in the MOPAC package.^[26,27] Dispersion interactions were considered and all calculations were carried out in vacuum. The reliability of the optimized structures was checked *via* frequency calculations based on density functional theory (DFT). There are no imaginary frequencies for the optimized geometries. The long side chains were substituted by H atoms to make the calculation feasible. The DFT functional ω B97XD was used, with the adoption of the 6-31G(d) basis set. The molecular orbitals were visualized using the Gauss View 6.0 software.



Scheme 1 Schematic representation for the cooperative supramolecular polymerization of the propeller-shaped monomer (*R*)-**1**, which displays fluorescent detection capability toward 2,6-dinitrotoluene.

Mass-balance Model for Supramolecular Polymerization

(*R*)-**1** adopt a cooperative supramolecular polymerization mechanism upon cooling or heating. The thermodynamical parameters of the polymerization of (*R*)-**1** are found by fitting CD spectroscopy data of melting curves with the one-component model for supramolecular polymerization. The fitted parameters for the (*R*)-**1** homopolymers are the enthalpy of elongation ΔH_e , the enthalpy of nucleation ΔH_n and the entropy term ΔS . The entropy term is same for nucleation and elongation. These parameters are related to the equilibrium constants of the elongation phase by:

$$K_e = \exp(-\Delta G_e/RT) \quad (1)$$

$$\text{with } \Delta G_e = \Delta H_e - T\Delta S \quad (2)$$

and of the nucleation phase (with nucleation penalty, NP) by

$$K_n = \sigma \times K_e \quad (3)$$

$$\text{with } \sigma = \exp(NP/RT) \quad (4)$$

$$NP = \Delta H_e - \Delta H_n \quad (5)$$

where ΔG_e is the Gibbs free energy of elongation, R is the gas constant, T is the absolute temperature, σ is the cooperativity parameter which is a ratio of the binding constant of nucleation (K_n) and elongation (K_e).

Synthesis of Compound (*R*)-**1**

The detailed procedure is listed in Scheme S1 (in ESI). Compounds **4** (52 mg, 0.08 mmol), **6** (226 mg, 0.25 mmol) and potassium *tert*-butoxide (27 mg, 0.24 mmol) were dissolved in *tert*-butanol (10 mL) and tetrahydrofuran (5 mL). The mixture was heated at 70 °C for 2 h. After cooling down to room temperature, the solvent was evaporated under reduced pressure, and the residue was extracted with water/dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated with a rotary evaporator. The residue was subjected to column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1, V/V) to afford (*R*)-**1** as a red solid (171 mg, 65%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 20 °C, δ , ppm): 7.73–7.71 (m, 6H), 7.66–7.61 (m, 15H), 7.53–7.42 (m, 17H), 7.13–7.11 (m, 4H), 7.08–7.04 (m, 3H), 6.97 (s, 6H), 6.24, 6.22 (d, 3H, $J=7.6$ Hz), 5.40–5.33 (m, 3H), 4.02–3.97 (m, 18H), 1.84–1.70 (m, 18H), 1.66, 1.64 (d, 9H, $J=6.8$ Hz), 1.50–1.43 (m, 18H), 1.26 (m, 144H), 0.89–0.86 (m, 27H). $^{13}\text{C-NMR}$ (101 MHz, CDCl_3 , 25 °C, δ , ppm): 160.8, 147.3, 139.4, 133.2, 132.4, 132.2, 131.8, 129.4, 127.5, 126.6, 124.5, 118.7, 117.7, 114.9, 108.7, 96.92, 83.0, 55.8. MALDI TOF-MS: m/z 3272.46 $[\text{M}+\text{H}]^+$.

Synthesis of Compound **2**

The synthetic procedure toward **2** was similar to that of (*R*)-**1**, by employing 4-methoxyphenylacetonitrile instead of compound **6** as the reactant (Scheme S2 in ESI). Compound **2** was obtained as a red solid (52.2 mg, 62%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 20 °C, δ , ppm): 7.59, 7.57 (d, 6H, $J=8.9$ Hz), 7.47–7.44 (m, 12H), 7.23 (s, 6H), 7.12, 7.09 (d, 6H, $J=8.7$ Hz), 6.96, 6.94 (d, 6H, $J=8.9$ Hz), 6.91–6.89 (m, 3H), 3.85 (s, 9H). $^{13}\text{C-NMR}$ (101 MHz, CDCl_3 , 25 °C, δ , ppm): 160.8, 147.2, 139.4, 133.1, 132.3, 132.2, 131.8, 129.4, 127.4, 126.5, 124.4, 118.6, 117.6, 114.8, 108.7, 96.9, 82.9, 55.8. MALDI TOF-MS: m/z 1034.23 $[\text{M}]^+$.

Crystal Structure Determinations

Single crystals of **2** suitable for X-ray structural analysis were

obtained by diffusing *n*-hexane into their THF solutions at room temperature. The X-ray diffraction data were collected on a Rigaku Smartlab (9 kW) X-ray diffractometer using Cu K α radiation ($\lambda=1.5406$ Å). The structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimization. The X-ray crystallographic coordinates for compound **2** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC 2189876. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk. Crystal data and processing parameters for **2** are summarized in Table S1 (in ESI).

RESULTS AND DISCUSSION

Structural and Spectroscopic Characterizations of the Model Compound **2**

We have firstly characterized the model compound **2** (Scheme 1) before studying supramolecular polymerization behaviors of (*R*)-**1**. Compound **2** keeps the inner D- π -A structure intact yet removes the peripheral units in (*R*)-**1**. The single crystal of **2** was obtained by slow diffusion of hexane vapor into the dichloromethane solution. As shown in Fig. 1(a), **2** crystallizes in the monoclinic space group C2/c with eight molecules per unit cell ($Z=8$, $a=44.58$ Å, $b=11.47$ Å, $c=28.20$ Å, and $\alpha=90^\circ$, $\beta=106.5^\circ$, $\gamma=90^\circ$). For the triphenylamine unit, the dihedral angles between the benzene rings are determined to be 65.71° , 63.69° and 73.72° , proving its propeller-shaped structure. Meanwhile, the dihedral angles between the thiophene and cyanostilbene groups are determined to be 16.53° , 16.49° and 16.52° , respectively. The results support the planarity of the “arm” segment in **2**. It is ascribed to the formation of non-covalent “conformational locks” between the thiophene and cyano units (Fig. 1b).^[28] The conclusion is supported by the S—N distances of 3.31, 3.06 and 3.21 Å in **2**, smaller than that of the S—N van der Waals distance (3.45 Å).^[29]

The two adjacent molecules in the crystal of **2** are arranged in a dimeric form (Fig. 1c), despite the absence of intermolecular π - π stacking interactions. It is reflected by the close C—H $\cdots\pi$ (2.86 Å), C—H $\cdots\text{CN}$ (2.63 Å) and C—H $\cdots\text{S}$ (2.91 Å) distances within the dimeric structure. Two dimers of **2** further interact with each other to form a tetrameric structure (Fig. 1d). It is driven by π - π stacking interactions (3.34 Å) between the adjacent “arm” segments, facilitating the formation of intermolecular charge transfer complex between the electron-rich thiophene and electron-poor cyanostilbene units.

Thanks to the D- π -A structural character, strong intra-molecular charge transfer (ICT) interaction exists in **2** to generate large dipole moment.^[30] In dilute CHCl_3 ($c=0.01$ mmol/L), **2** displayed a broad absorption band between 320 and 510 nm ($\lambda_{\text{max}}=443$ nm, Fig. S1 in ESI). By calculating the HOMO and LUMO orbital distributions (Fig. S2 in ESI), it is evident that charge transfer exists from the electron-rich thiophene and triphenylamine to the electron-poor cyanostilbene groups. The ICT interaction rendered solvatochromic behaviors to **2**. Upon increasing the solvent polarity, the fluorescent maxima red-shifted from 506 nm in toluene (green emission colour) via 557 nm in CHCl_3 (yellow emission color) to 644 nm in DMF (red emission color) (Fig. 2). In the meantime, the ab-

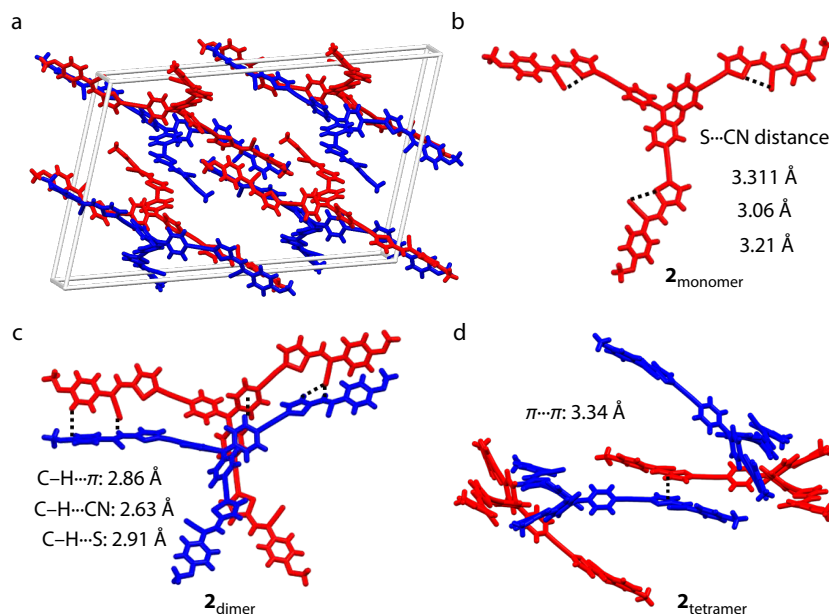


Fig. 1 (a) Molecular packing of **2** in the crystal viewed along the *b* axis. (b) Top view of the monomer structure selected from the **2** single crystal structure. The S—N distances of 3.31 Å, 3.06 Å, and 3.21 Å in **2** indicate the formation of non-covalent “conformational locks” between the thiophene and cyano units. (c) Top view of the dimer packing form in the crystal of **2**. (d) Side view of the tetrameric structure in the crystal of **2**, which is driven by π - π stacking interactions (3.34 Å) between the adjacent two dimers of **2** (CCDC: 2189876).

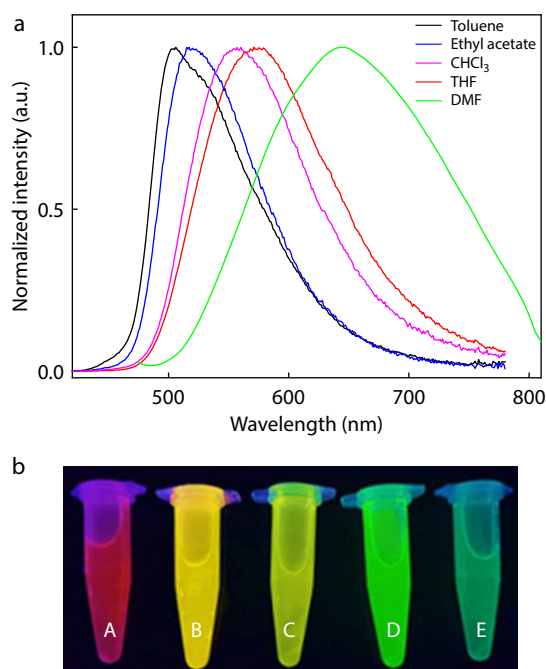


Fig. 2 (a) Normalized fluorescence spectra of **2** ($c=0.01$ mmol/L) in different solvents; (b) Photographs of **2** in different solvents (A: DMF; B: THF; C: CHCl_3 ; D: ethyl acetate; E: toluene) under 365 nm UV light.

sorption bands hardly changed in these solvents (Fig. S1 in ESI). Accordingly, the solvatofluorochromic phenomena of **2** originated from the different stability of ground and excited states in the examined solvents.

Supramolecular Polymerization Behaviors of (*R*)-**1**

We then studied supramolecular assembly behaviors of the propeller-shaped compound (*R*)-**1**. As widely documented,

chlorinated solvents are benign for the π -conjugated molecules in solution, while both hydrogen bonding and π - π stacking interactions are favorable in apolar media.^[16] In dilute CHCl_3 ($c=0.01$ mmol/L), (*R*)-**1** exhibited the maximum absorption at 428 nm ($\epsilon=1.61\times 10^5$ L·cm⁻¹·mol⁻¹, Fig. 3a). Depending on DFT calculations (Fig. S3 in ESI), the HOMOs of (*R*)-**1** were mainly distributed over the central donor cores (thiophene and triphenylamine unites), while the LUMOs were dominated by the acceptor groups, giving rise to ICT effect for the D-A units. No Cotton effect was detected for (*R*)-**1** in CHCl_3 (Fig. 3b), illustrating the dominance of the molecularly dissolved state. Upon switching the solvent to methylcyclohexane (MCH)/toluene ($V/V=3/1$), a shoulder band emerged between 468 and 536 nm (Fig. 3a). Meanwhile, a strong Cotton effect was observed in the ICT absorption region (Fig. 3b), with a negative maximum at 475 nm ($\Delta\epsilon=-97$ L·cm⁻¹·mol⁻¹; anisotropy factor $g=-0.00012$) and a positive one at 375 nm ($\Delta\epsilon=42$ L·cm⁻¹·mol⁻¹; $g=0.00065$). These results indicate chirality transfer from the stereogenic *N*-[(1*R*)-phenylethyl] benzamides to the inner triphenylamine cyanostilbene core, leading to the formation of helical supramolecular aggregates in MCH/toluene ($V/V=3/1$).

Deeper insights into supramolecular assembly mechanism were achieved *via* temperature-dependent spectroscopic measurements. Upon heating the MCH/toluene solution ($V/V=3/1$) of (*R*)-**1** to 80 °C, the absorbance signals (Fig. S4 in ESI) resembled that in CHCl_3 , reflecting the dominance of un-aggregated monomers. By varying the temperature between 30 and 80 °C, two isosbestic points appeared in UV-Vis spectra ($\lambda=385$ and 470 nm, Fig. S4 in ESI). Meanwhile, the CD signals disappeared at 80 °C and recovered after cooling (Fig. 3b). These results suggested a reversible transition between the monomeric and supramolecular aggregated states. When monitoring the CD intensities of (*R*)-**1** at 490 nm as a function of temperature, a non-sigmoidal melting curve was obtained

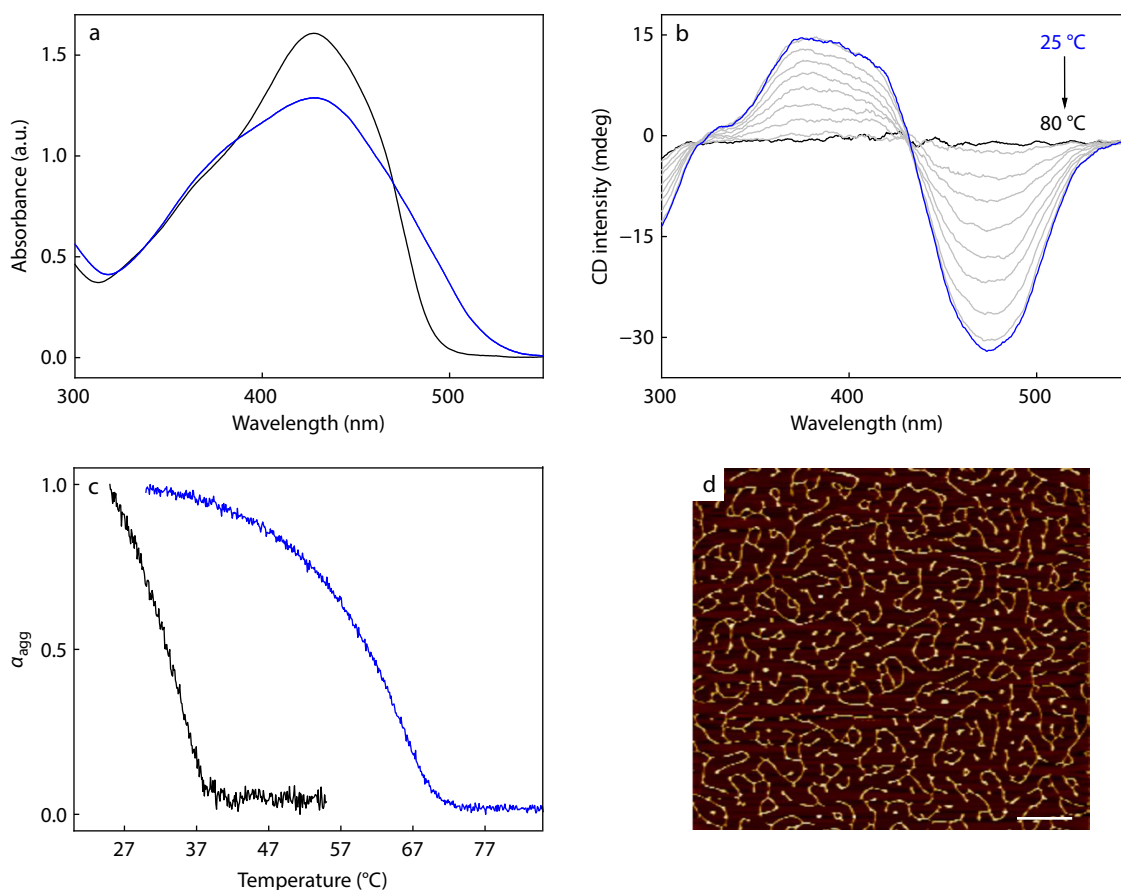


Fig. 3 (a) UV-Vis spectra of (*R*)-**1** ($c = 0.01$ mmol/L, 25 °C) in CHCl₃ (black line) and MCH/toluene (V/V=3/1, blue line). (b) CD spectra ($c=0.01$ mmol/L, 10 mm cuvette) of (*R*)-**1** in MCH/toluene (V/V=3/1) at 25 °C (blue solid line) and 80 °C (black solid line). The arrows show spectral changes of the CD spectra upon heating from 25 °C to 80 °C. (c) Normalized CD intensities of (*R*)-**1** in MCH/toluene (V/V=3/1, $c=0.01$ mmol/L, blue line) and MCH/toluene (V/V=1/1, $c=0.01$ mmol/L, black line) versus temperature at the cooling rate of 1 °C·h⁻¹. (d) AFM image of (*R*)-**1** on mica. Scale bar: 3 μ m.

(Fig. 3c). Plots of the degree of aggregate (α_{agg}) against temperature indicated the adoption of a cooperative nucleation-elongation mechanism for the supramolecular assembly process. The critical elongation temperature (T_e) was determined to be 68.4 °C (MCH/toluene=3/1, V/V, Fig. 3c). Remarkably, the melting curves of (*R*)-**1** overlapped between the heating and cooling processes. The absence of hysteresis demonstrates that the supramolecular assembly process is under thermodynamic control.

We have applied a one-component equilibrium model to fit the melting curves.^[31] Accordingly, the thermodynamic parameters were acquired for the supramolecular polymerization process of (*R*)-**1** (Table 1 and Fig. S5 in ESI). The enthalpy value (ΔH_e) was determined to be -99.0 kJ·mol⁻¹, while the entropy (ΔS) value was -0.192 kJ·mol⁻¹·K⁻¹. It provided the Gibbs free energy change (ΔG_e) of -41.8 kJ·mol⁻¹ at 25 °C. Accordingly, the supramolecular assembly process of (*R*)-**1** was enthalpy driven. The cooperativity factor σ was determined to be 2.4×10^{-3} , giving rise to the nucleation penalty (NP) of -14.9 kJ·mol⁻¹. The number-averaged degree of polymerization value of (*R*)-**1** in MCH/toluene (V/V=3/1, $c=0.01$ mmol/L) was calculated to be 300 at 25 °C (Fig. S6 in ESI). It unambiguously supports the formation of long-range ordered supra-

molecular polymers because of the adoption of cooperative self-assembly mechanism. The conclusion was further supported by atomic force microscopy (AFM), which showed the formation of 1D nanofibers for (*R*)-**1** with a length of a few microns (Fig. 3d).

Elucidation the Stacking Mode in Supramolecular Polymeric State

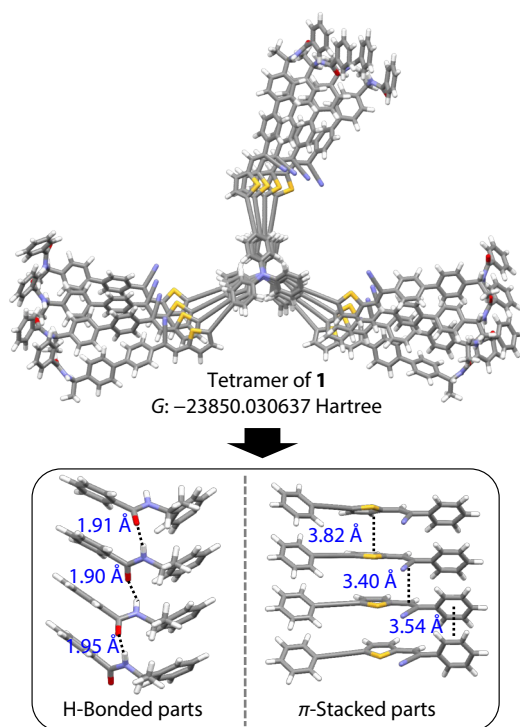
We then performed theoretical calculations to clarify the stacking modes between the neighbouring monomers. Geometries of the tetrameric structures of (*R*)-**1** were optimized *via* the semi-empirical PM7 method. The peripheral alkyloxy chains on (*R*)-**1** were replaced by the hydrogen atoms. For the optimized geometry of the tetrameric structure (*R*)-**1**₄ (Fig. 4), the NH—O bond lengths between the neighbouring amide units are 1.91, 1.90 and 1.95 Å, with the N—H—O bond angles of 169.9°, 160.3° and 169.8°, respectively. The close NH—O distances demonstrate the presence of hydrogen bonding interactions in supramolecular polymers. The inner triphenylamine units were arranged in a face-to-face manner, with the intermolecular π - π distance of 3.40–3.82 Å. Hence, intermolecular π - π stacking interactions might also contribute to the supramolecular stacking process.

To validate the importance of hydrogen bonding driving

Table 1 Thermodynamic parameters for supramolecular polymerization of **1** by fitting CD data.

(<i>R</i>)- 1	T_e (°C)	ΔH_e (kJ·mol ^{−1})	ΔS (kJ·mol ^{−1})	ΔG_{298K} (kJ·mol ^{−1})
3:1 ^a	68.4	−99.0	−0.192	−41.8
1:1 ^b	39.7	−89.6	−0.191	−32.7

^a Acquired for (*R*)-**1** in MCH/toluene (V/V=3/1, c=10 μmol/L); ^b Acquired for (*R*)-**1** in MCH/toluene (V/V=3/1, c=10 μmol/L).

**Fig. 4** Top view of the optimized tetrameric structure of (*R*)-**1**. Side view of π -stacked and H-bonded parts in tetramer of (*R*)-**1**. The energy calculations were calculated by DFT with the ω B97XD/6-31G(d) level of theory.

forces, we compared the supramolecular polymerization behaviour of (*R*)-**1** in toluene, MCH/toluene (V/V=1/1) and MCH/toluene (V/V=3/1). As widely documented, hydrogen bonding strength weakens in polar media. In pure toluene, the absence of Cotton effect suggested the dominance of the monomeric species.^[32] Although Cotton effects were present in MCH/toluene (V/V=1/1, Fig. S7a in ESI), the intensities were lower than those in MCH/toluene (V/V=3/1) (anisotropy factor g value at 475 nm: −0.00009 versus −0.00012). As shown in Table 1, both the ΔH_e and ΔG_e values of (*R*)-**1** in MCH/toluene (V/V=1/1, Fig. S7b in ESI) were lower than those in MCH/toluene (V/V=3/1). The results indicate weakening of hydrogen bonding strength by increasing the volume fraction of toluene in MCH. The impact of hydrogen bonding strength can be further reflected by the decreased T_e value in MCH/toluene (V/V=1/1) than that in MCH/toluene (V/V=3/1) (39.7 °C versus 68.4 °C, Fig. 3c). Accordingly, supramolecular polymers showed lower thermal stability upon increasing the solvent polarity.

We further analysed the energy difference between the monomeric and tetrameric structures. Depending on DFT cal-

culations, the energy of monomer and tetramer were determined to be −5962.367549 Hartree and −23850.030637 Hartree, respectively. Apparently, the tetramer energy was lower than that of the quadruple monomer in gas phase (Fig. S8 in ESI), ascribed to the participation of multivalent hydrogen bonding and π - π stacking interactions in **1**₄ (ΔG = 352 kcal/mol).

Fluorescent Detection of 2,6-Dinitrotoluene for the Supramolecular Polymers of (*R*)-**1**

Temperature-dependent fluorescent measurements were performed for (*R*)-**1** in MCH/toluene solution (V/V=3/1, c=0.01 mmol/L). At 90 °C (dominated by the monomeric state), a weak green emission was observed ($\lambda_{\max}$ =502 nm, Fig. S9 in ESI). In stark contrast, a bright yellow emission colour appeared at 25 °C (dominated by the supramolecular polymeric state), accompanied by red-shifting of the emission maximum ($\lambda_{\max}$ =557 nm, Fig. S9 in ESI). It is evident that the supramolecular polymeric state displayed enhanced emission intensity than that in the monomeric state. The emission enhancement is ascribed to the suppression of free bond rotations, giving rise to the reduction of non-radiative decay rate in the supramolecular polymeric state.

On this basis, we studied guest encapsulation capability of the resulting supramolecular polymers. Upon gradual addition of 2,6-DNT, the CD signal of (*R*)-**1** maintained (Fig. S12 in ESI), while the emission intensity of (*R*)-**1** at 557 nm progressively decreased in MCH/toluene (V/V=3/1) (Fig. 5a). It supports the intercalation of 2,6-DNT into the supramolecular polymeric stacks of (*R*)-**1**. With the presence of four equivalent amount of 2,6-DNT, the fluorescence of (*R*)-**1** was quenched by 78.9% [quenching efficiency, $(I_0 - I)/I_0 \times 100\%$, where I_0 and I are emission intensity of (*R*)-**1** at 557 nm before and after addition of 2,6-DNT, respectively]. The quenching efficiency increased to 86.6% for the (*R*)-**1** supramolecular polymers in the film state (Fig. S11 in ESI). In sharp contrast, the fluorescence quenching efficiency was determined to be 45.5% for the monomeric state of (*R*)-**1** toward 2,6-DNT (Fig. S10 in ESI). The severe emission quenching in the supramolecular polymeric state than that in the monomeric state originated from the signal collection and amplification effects. Hence, supramolecular polymers of (*R*)-**1** served as an effective “turning-off” fluorescent probe toward 2,6-DNT.

In principle, emission quenching arises from photoinduced electron transfer and/or energy transfer. Since no spectral overlapping exists between the emission spectrum of 2,6-DNT and the absorption spectrum of (*R*)-**1**, it can be concluded that energy transfer plays a negligible role. Alternatively, photo-induced electron transfer prevails in the current system, as proved by DFT calculations (Fig. 5b). In particular, the LUMO levels of (*R*)-**1** were determined to be −0.75 eV, higher than that of 2,6-DNT (−0.87 eV). The small gap indicates strong tendency of electron transfer from the excited fluorophores to the analytes. Accordingly, the excited electron of (*R*)-**1** was converted to the LUMO of the electron-poor 2,6-DNT. It eventually returns to the ground state by non-radiative transition. The radiative electronic transition was severely blocked, leading to the emission quenching phenomenon.

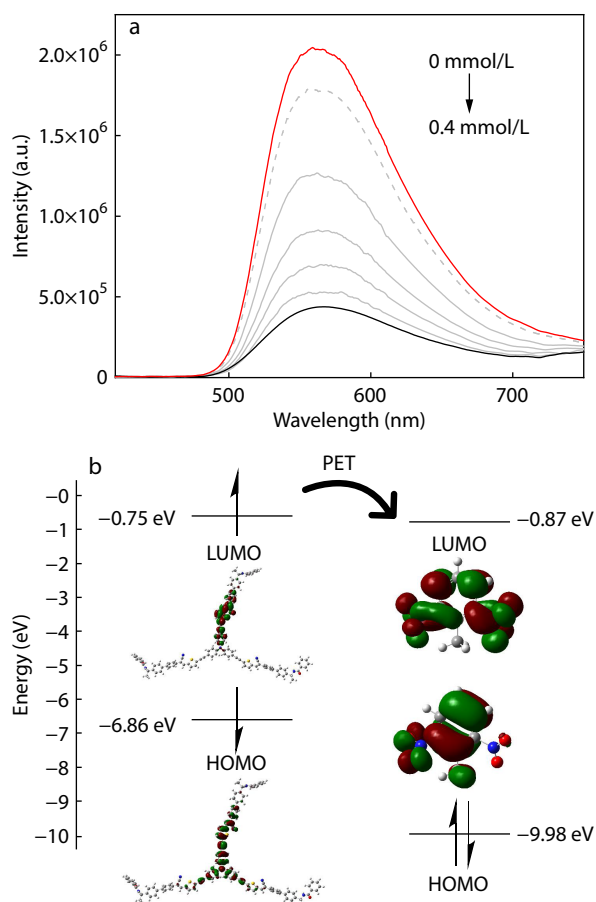


Fig. 5 (a) Fluorescent spectra of (R)-1 in MCH/toluene (V/V=3/1, $c=0.01$ mmol/L) at 25 °C with the gradually addition of 0 mol% (red line) and 400 mol% (black line) amounts of 2,6-dinitrotoluene; (b) DFT calculated energy levels showing possible electronic process for fluorescence quenching of (R)-1 by 2,6-dinitrotoluene.

CONCLUSIONS

In summary, we have constructed a novel type of supramolecular polymers on the basis of D- π -A triphenylamine cyanostilbene compound (R)-1. The propeller shape of triphenylamine cyanostilbenes is proved by the single crystal of the model compound **2**. Thanks to the participation of three-fold hydrogen bonds between the neighbouring monomers, (R)-1 forms long-range-ordered supramolecular polymers via the nucleation-elongation cooperative mechanism. The supramolecular polymeric state displays amplified chirality and enhanced emission than those in the monomeric state. The resulting supramolecular polymers derived from (R)-1 exhibit severe emission quenching upon addition of 2,6-DNT as the encapsulated guest, ascribed to photoinduced electron transfer from the triphenylamine cyanostilbene fluorophore to the explosive analyte. The current study demonstrates the feasibility to supramolecular polymerize propeller-like π -conjugated molecules via the rational molecular design. It brings rich photophysical properties and electron delocalization characteristics at the supramolecular level, which would be beneficial for applications in sensors and optoelectronic materials.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-023-2917-3>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 21922110 and 21871245), the Collaborative Innovation Program of Hefei Science Center, CAS (No. 2022HSC-CIP014), and the Fundamental Research Funds for the Central Universities (No. WK3450000005). We are grateful for the technical support from the High Performance Computing Center of University of Science and Technology of China for DFT and TD-DFT computations.

REFERENCES

- Mako, T. L.; Racicot, J. M.; Levine, M. Supramolecular luminescent sensors. *Chem. Rev.* **2019**, *119*, 322–477.
- Xu D. A.; Zhou, Q. Y.; Dai, X.; Ma, X. K.; Zhang, Y. M.; Xu, X.; Liu, Y. Cucurbit[8]uril-mediated phosphorescent supramolecular foldamer for antibiotics sensing in water and cells. *Chin. Chem. Lett.* **2022**, *33*, 851–854.
- Yin, Z. H.; Yang, Y. C.; Yang, J. P.; Song, G. B.; Hu, H.; Zheng, P.; Xu, J. F. Supramolecular polymerization powered by *escherichia coli*: fabricating a near-infrared photothermal antibacterial agent *in situ*. *CCS Chem.* **2022**, *4*, 3285–3295.
- Yin, Z. H.; Song, G. B.; Jiao, Y.; Zheng, P.; Xu, J. F.; Zhang, X. Dissipative supramolecular polymerization powered by light. *CCS Chem.* **2019**, *1*, 335–342.
- Liu, K.; Jiang, Y. W.; Bao, Z.; Yan, X. Skin-inspired electronics enabled by supramolecular polymeric materials. *CCS Chem.* **2019**, *1*, 431–447.
- Wu, G. L.; Li, F.; Tang, B. H.; Zhang, X. Molecular engineering of noncovalent dimerization. *J. Am. Chem. Soc.* **2022**, *144*, 14962–14975.
- Jia, D.; Zhong, H.; Jiang, S.; Yao, R.; Wang, F. Simultaneous enhancement of phosphorescence and chirality by host-guest recognition of molecular tweezers. *Chin. Chem. Lett.* **2022**, *33*, 4900–4903.
- Yuan, W.; Cheng, J. J.; Li, X. P.; Wu, M. J.; Han, Y.; Yan, C. M.; Zou, G.; Müllen, K.; Chen, Y. L. 5,6,12,13-Tetraazaperopyrenes as unique photonic and mechanochromic fluorophores. *Angew. Chem. Int. Ed.* **2020**, *59*, 9940–9945.
- Dumele, O.; Chen, J. H.; Passarelli, J. V.; Stupp, S. I. Supramolecular energy materials. *Adv. Mater.* **2020**, *32*, 1907247.
- Han, Y.; Zhang, X.; Ge, Z.; Gao, Z.; Liao, R.; Wang, F. A bioinspired sequential energy transfer system constructed via supramolecular copolymerization. *Nat. Commun.* **2022**, *13*, 3546.
- Zhang, X. Supramolecular polymer chemistry: past, present, and future. *Chinese J. Polym. Sci.* **2022**, *40*, 541–542.
- Li, Z.; Han, Y.; Nie, F.; Liu, M.; Zhong, H.; Wang, F. Bright and robust phosphorescence achieved by non-covalent clipping. *Angew. Chem. Int. Ed.* **2021**, *60*, 8212–8219.
- Qian, W. R.; Zuo, M. Z.; Niu, P. B.; Hu, X. Y.; Wang, L. Y. The construction of aggregation-induced charge transfer emission

- systems in aqueous solution directed by supramolecular strategy. *Chin. Chem. Lett.* **2022**, *33*, 1975–1978.
- 14 Gao, Z.; Tian, Y.; Hsu, H.; Han, Y.; Chan, T.; Wang, F. Additive-controlled kinetic trapping of quadruple platinum(II) stacks with emergent photothermal behaviors. *CCS Chem.* **2021**, *3*, 105–115.
 - 15 Korlepara, D. B.; Henderson, W. R.; Castellano, R. K.; Balasubramanian, S. Differentiating the mechanism of self-assembly in supramolecular polymers through computation. *Chem. Commun.* **2019**, *55*, 3773.
 - 16 Liao, R.; Wang, F.; Guo, Y.; Han, Y.; Wang, F. Chirality-controlled supramolecular donor-acceptor copolymerization with distinct energy transfer efficiency. *J. Am. Chem. Soc.* **2022**, *144*, 9775–9784.
 - 17 Xue, Y.; Jiang, S.; Zhong, H.; Chen, Z.; Wang, F. Photo-induced polymer cyclization via supramolecular confinement of cyanostilbenes. *Angew. Chem. Int. Ed.* **2022**, *61*, e202110766.
 - 18 de Greef, T. F. A.; Smulders, M. M. J.; Wolffs, M.; Schenning, A.; Sijbesma, R. P.; Meijer, E. W. Supramolecular polymerization. *Chem. Rev.* **2009**, *109*, 5687–5754.
 - 19 Han, Y.; Yin, Y.; Wang, F.; Wang, F. Single-photon near infrared responsiveness from molecular to supramolecular levels via platination of pentacenes. *Angew. Chem. Int. Ed.* **2021**, *60*, 14076.
 - 20 Gao, Z.; Han, Y.; Wang, F. Cooperative supramolecular polymers with anthracene–endoperoxide photo-switching for fluorescent anti-counterfeiting. *Nat. Commun.* **2018**, *9*, 3977.
 - 21 Casellas, N. M.; Pujals, S.; Bochicchio, D.; Pavan, G. M.; Torres, T.; Albertazzi, L.; García-Iglesias, M. From isodesmic to highly cooperative: reverting the supramolecular polymerization mechanism in water by fine monomer design. *Chem. Commun.* **2018**, *54*, 4112–4115.
 - 22 Ślęczkowski, M. L.; Mabesoone, M. F. J.; Ślęczkowski, P.; Palmans, A. R. A.; Meijer, E. W. Competition between chiral solvents and chiral monomers in the helical bias of supramolecular polymers. *Nat. Chem.* **2020**, *13*, 200–207.
 - 23 Picini, F.; Schneider, S.; Gavat, O.; Vargas Jentzsch, A.; Ta, J. J.; Maaloum, M.; Strub, J. M.; Tokunaga, S.; Lehn, J. M.; Moulin, E.; Giuseppone, N. Supramolecular polymerization of triarylamine based macrocycles into electroactive nanotubes. *J. Am. Chem. Soc.* **2021**, *143*, 6498.
 - 24 Wang, Q. H.; Zhong, Y. L.; Mille, D. P.; Lu, X. X.; Tang, Q.; Lu, Z. L.; Zurek E.; Liu R.; Gong, B. Self-assembly and molecular recognition in water: tubular stacking and guest-templated discrete assembly of water-soluble, shape-persistent macrocycles. *J. Am. Chem. Soc.* **2020**, *142*, 2915–2924.
 - 25 Kim, T.; Mori, T.; Aida, T.; Miyajima, D. Dynamic propeller conformation for the unprecedentedly high degree of chiral amplification of supramolecular helices. *Chem. Sci.* **2016**, *7*, 6689–6694.
 - 26 Stewart, J. J. P. Optimization of parameters for semiempirical methods VI: more modifications to the NDDO approximations and reoptimization of parameters. *J. Mol. Model.* **2013**, *19*, 1–32.
 - 27 James, J. P. Stewart. MOPAC2016; Stewart Computational Chemistry. <http://openmopac.net/>.
 - 28 Huang, H.; Chen, Z. H.; Ortiz, R. P.; Newman, C.; Usta, H.; Lou, S.; Youn, J.; Noh, Y. Y.; Baeg, K. J.; Chen, L. X.; Facchetti, A.; Marks, T. J. Combining electron-neutral building blocks with intramolecular “conformational locks” affords stable, high-mobility p and N-channel polymer semiconductors. *J. Am. Chem. Soc.* **2012**, *134*, 10966–10973.
 - 29 Rowland, R. S.; Taylor, R. J. Intermolecular nonbonded contact distances in organic crystal structures: comparison with distances expected from van der Waals radii. *Phys. Chem.* **1996**, *100*, 7384.
 - 30 Sun, Z. B.; Li, S. Y.; Liu, Z. Q.; Zhao, C. H. Triarylborane π -electron systems with intramolecular charge-transfer transitions. *Chin. Chem. Lett.* **2016**, *27*, 1131–1138.
 - 31 Zhao, D. H.; Moore, J. S. Nucleation-elongation: a mechanism for cooperative supramolecular polymerization. *Org. Biomol. Chem.* **2003**, *1*, 3471–3491.
 - 32 Wagner, W.; Wehner, M.; Stepanenko, V.; Würthner, F. Impact of molecular shape on supramolecular copolymer synthesis in seeded living polymerization of perylene bisimides. *CCS Chem.* **2019**, *2*, 598–613.