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Introduction

Intensive research has been performed in π -conjugated molecular systems in the past few decades owing to their unique optical properties.¹ A notorious problem for π -conjugated systems is the formation of excimers or exciplexes via $\pi - \pi$ stacking interactions in the aggregation state, which often causes fluorescence quenching, namely, the aggregation-caused quenching (ACQ).²⁻⁴ This problem used to be overcome by a complicated construction strategy until an opposite phenomenon, AIE, was discovered.⁵ The molecules with the AIE property have weak fluorescence in the solution, but their fluorescence is enhanced by several orders on the formation of aggregates.^{6,7} The discovery of the AIE property is beyond doubt a milestone in the research on π -conjugated systems because it provides a brand new view of the relationship between aggregation of molecules and light-emission properties. With this important discovery, the previously dominant ACQ phenomenon is now found to represent only the tip of the iceberg. The whole

Valine-containing silole: synthesis, aggregationinduced chirality, luminescence enhancement, chiral-polarized luminescence and self-assembled structures

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The synthesis of valine-containing silole is reported. The introduction of a chiral valine pendant to silole endows the new compound (1 in Scheme 1) with not only circular dichroism (CD) and chiral-polarized luminescence (CPL), but also an aggregation-induced emission (AIE) property. The AIE effect boosts the fluorescence quantum efficiency, $\Phi_{\rm F}$, from 0.33% in pure THF to a maximum of 18.9% when water is added, which is 57 times higher than that in pure THF. In the thin film state, the $\Phi_{\rm F}$ value measured by a calibrated integrating sphere can reach 80.3%, which is 243 times higher than that in the solution state. The amphiphilic valine attachments enable the compound to aggregate into complex architectures by a self-assembling process as revealed by AFM images. This compound self-assembles into helical fibers on the evaporation of its THF solution, which corresponds well with its CD and CPL properties. The addition of a poor solvent such as water or hexane to the THF solution also leads to the formation of aggregated structures, which exhibit helical enhancement or inversion in handedness to different extents.

> underlying mechanism of aggregation and luminescence is now clearly re-elucidated.⁸ When the planar π -conjugated molecules aggregate in a face-to-face stacking manner, non-irradiative energy transfer would take place to make the luminescence lower or even quenched. However, for the non-planar π -conjugated molecules, when aggregation does not occur in a face-toface manner, aggregation will efficiently hinder the intermolecular rotation and help enhance the luminescence efficiency.9 Most optical devices are used in the solid state; thus, AIE molecules are ideal candidates for the fabrication of highly efficient devices because of their high luminescence efficiency in the aggregation state. Silole, which is the most famous AIE molecule, is a propeller-shaped, π -conjugated molecule with extremely high quantum yield in the solid state; moreover, it has an important potential application as a material for fabricating optical sensors.10 Fabricating novel silole molecules with the AIE property into highly ordered nano-architectures would be desirable because of the increasing demand for the miniaturization of devices. However, without structural modification, silole can only self-assemble into nanoparticles due to its lack of fruitful functional groups that can realize complex self-assembling processes. Thus, it is necessary to modify the silole core with proper peripheries that are capable of judicious assembling.

> Helical architectures are among the most exciting classes of self-assembled structures.⁷ It has been recognized that the introduction of chiral amino acid to π -conjugated systems can



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efficiently induce the formation of helical conformation and helical aggregates.8 A hybrid of chirality with AIE property might simultaneously give offspring molecules, which bear helical sense, luminescence and chiral-polarized luminescence property.9 Inspired by this idea, we incorporate valine attachments in silole and synthesize a chiral silole containing two valine attachments (Scheme 1). The chiral carbon of valine attachments is expected to exert an asymmetric force on the silole core in order to induce a helical conformation.¹⁰ Hydrogen bonds between the amino acid attachments and the solvophobic effect of the amphiphilic molecules help stabilize the helical conformation. Therefore, besides the AIE property, compound 1 is also expected to possess both CD and CPL properties. Moreover, the existence of amphiphilic valine attachments also endues the compound with the ability to accomplish judicious selfassembling processes.

Herein, we report the synthesis, optical properties and selfassembling behavior of **1**. Compound **1** showed AIE, CD and CPL properties, and it also had the capacity to self-assemble into helical architectures on evaporation of solvent or by addition of a poor solvent such as water and hexane. These results help to broaden the view of AIE molecular design and also provide important insight for using AIE molecules as the building blocks for the fabrication of novel devices with CPL and luminescence properties.

Experimental section

Materials

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl in an atmosphere of nitrogen immediately prior to use. Copper(1) iodide, $ZnCl_2 \cdot TMEDA$, triphenylphosphine, dichlorobis(triphenylphosphine)palladium(11), and other chemicals and solvents were all purchased from Aldrich and used as received without further purification. 1,1-Dimethyl-2,5bis[4-(azidomethyl)phenyl]-3,4-diphenylsilole (2) and (4-ethynylbenzoyl-L-valine (1*S*,2*R*,5*S*)-(+)-menthyl ester) (3) were prepared according our previous papers.^{11,12}

Instrumental analysis

¹H and ¹³C NMR spectra were measured on a Bruker ARX 400 NMR spectrometer using chloroform-d as the solvent and tetramethylsilane (TMS) as the internal reference. UV absorption spectra were obtained on a Milton Ray Spectronic 3000 array

spectrophotometer. CD spectra were recorded on a JASCO J-810 spectropolarimeter in a 1 mm quartz cuvette using a step resolution of 0.1 nm, a scan speed of 100 nm min⁻¹, a sensitivity of 0.1 nm, and a response time of 0.5 s. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Emission efficiencies of thin films of the molecules were measured by a calibrated integrating sphere. High-resolution mass spectra (HRMS) were measured on a GCT Premier CAB 048 mass spectrometer operating in an electron-ionization or a MALDI-TOF mode. Circular photoluminescence spectra were measured with a home-made CPL spectroscopy system.11,13 The system is composed of a 325 nm He-Cd laser as the light source, a photo-elastic modulator (Hinds, PEM-90, 50 kHz), a broadband Glan-laser polarizer (Special Optics) oriented at 45° to the PEM optical axis, a monochromator (SPEX 500 M) and a photomultiplier tube (PMT, Hamamatsu, R928). An excitation laser of 325 nm in wavelength was irradiated on the sample from the same side of emission collection. A UV depolarizer was employed on the excitation light to avoid unnatural CPL. The retardation of the emitted light was controlled by the quarterwave 50 kHz modulator PEM-90 and detected by the photomultiplier tube after passing through the linear polarizer. The DC component of the PMT output was measured by a digital multimeter (Thurlby 1905a), whereas the AC component with a frequency of 50 kHz was amplified by a pre-amplifier (Stanford Research Systems, SR560) and analyzed by a lock-in amplifier (Stanford Research Systems, SR510). The CPL dissymmetry factor, $g_{\rm em} = 2(I_{\rm L} - I_{\rm R})/(I_{\rm L} + I_{\rm R})$, was evaluated from the ratio of the AC signal to the DC signal.

The AFM samples were prepared by dropping a small drop of a diluted solution of 1 on the surface of newly cleaved mica under ambient conditions. After 5 min of incubation, the sample was dried with nitrogen gas. The images were collected with a Nanoscope atomic force microscope (Icon) operating in a tapping mode using hard silicon tips with a spring constant of ~40 N m⁻¹.

Synthesis

Synthesis of 1. In a 50 mL round-bottom flask equipped with a reflux condenser, 0.105 g (0.2 mmol) of 2 and 0.192 g (0.5 mmol) of 3 were added to 15 mL of water-THF-ethanol mixture (1/1/1, v/v/v). Then, 0.5 mL of freshly prepared 1 M aqueous solution of sodium ascorbate was added, followed by 7.5 mg (0.03 mmol) of copper(II) sulfate in 0.1 mL of water. The solution was stirred vigorously at 70 °C overnight. After being cooled to room temperature, 50 mL of water was added, and the reaction mixture was extracted with DCM. The combined organic layer was washed with brine and water. After solvent evaporation under reduced pressure, the residue was purified by a silica gel column using ethyl acetate as the eluent. A yellow solid was obtained in 95.6% yield. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.86 (m, 8H), 7.71 (s, 2H), 7.06 (d, 4H), 7.00 (m, 6H), 6.93 (d, 4H), 6.77 (m, 4H), 6.67 (d, 2H), 5.48 (s, 4H), 4.79 (m, 2H), 4.73 (d, 2H), 2.33 (d, 2H), 2.03 (d, 2H), 1.92 (m, 2H), 1.72 (m, 4H), 1.45 (m, 2H), 1.05 (d, 10H), 0.96 (d, 7H), 0.90 (d, 15H), 0.75 (d, 6H), 0.46 (s, 6H). ¹³C NMR (100 MHz, CDCl₃), δ (TMS, ppm):

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171.9, 166.9, 141.2, 129.9, 129.6, 127.9, 127.8, 127.6, 125.8, 76.1, 57.8, 46.9, 40.9, 34.2, 31.8, 31.5, 26.1, 22.9, 22.0, 21.0, 19.6, 17.4, 15.8, 2.2, 0.1, -3.7. HRMS (MALDI-TOF): m/z 1290.7086 (M⁺, calcd 1290.7066).

Results and discussion

Material preparation and structural characterization

In order to synthesize π -conjugated molecules with chiroptical properties and strong solid-state light emission, we chose silole as the AIE luminophore and valine as the chiral attachment, which was synthesized with an azide–alkyne click route. Our rich experiences in click¹⁴ and silole¹⁵ chemistries allowed us to readily carry out this synthesis. Diazide-functionalized silole (2) and amino acid derivative (3) were synthesized following our previously published procedures.^{11,12} The click reaction of two equivalents of 2 and 3 was catalyzed by CuSO₄/sodium ascorbate (Scheme 1), affording 1 in excellent yield (see Experimental section for detailed procedures).

The resultant **1** was characterized by standard spectroscopic techniques, including ¹H NMR, ¹³C NMR, and HRMS, from which satisfactory analysis data corresponding to its expected chemical structure were obtained (see Experimental section for detailed spectroscopic data).

UV absorption and CD spectra

The UV absorption spectrum of **1** is shown in Fig. 1A. In THF, compound **1** exhibits two absorption bands located at 350 and 279 nm, corresponding to the absorptions of the silole core and the peripheral triazolylphenyl rings, respectively.^{11,12} We then investigated its optical activity by CD spectroscopy. As can be seen in Fig. 1B, the isolated molecules of **1** in the THF solution show only very weak CD signals in the absorption region of the triazolylphenyl ring. However, film casting by solvent evaporation leads to the emergence of Cotton effect at 249, 280 and 375 nm. Since the chiral unit (**3**) is CD silent at any wavelength longer than 300 nm,¹² the peak at 375 nm should be associated with the absorption transition of the silole core, unambiguously proving that chiral pendants induce the silole cores to be arranged helically with a preferred screw sense. This shows an interesting chiral transcription process from the chiral



Fig. 1 (A) Normalized UV absorption spectrum of 1 in THF. (B) CD spectra of 1 in 1,2-dichloroethane solution with a concentration of 10^{-4} M and drop cast film from a 1,2-dichloroethane solution of 1 (2 mg mL⁻¹).

pendants to the nonchiral luminophoric cores. Furthermore, in the solution, almost no CD signals are observed; however, on molecular aggregation (film state), strong CD signals appear and display aggregation-induced circular dichroism (AICD).¹¹

Aggregation-induced emission

It is known that conventional conjugated molecules generally suffer from the ACQ effect in the solid state, which has become a thorny problem in the development and fabrication of efficient organic light-emitting diodes and biological fluorescent kits.¹⁶ The π - π stacking interaction between the conjugated chiral molecules normally serves as a dominant force that drives the self-assembling process to form hierarchical structures. However, the accompanying ACQ effect induced by the intermolecular excitonic coupling between the adjacent luminophores plays a role in remarkably weakening the light emission. Thus, developing luminophores with high efficiency in the solid state are highly demanded. The AIE luminogens may be ideal candidates for the fabrication of highly efficient devices with both CD and CPL properties because they exhibit enhanced luminescent efficiency and high spectral stability in the aggregate state.

To check whether **1** is AIE-active, we investigated the PL spectra of **1** in THF-water mixtures with different water fractions (f_w). When excited at 360 nm, the PL curve of **1** in THF solution shows almost a flat line parallel to the abscissa (Fig. 2A), suggesting that it is nonemissive when the molecules dissolve in the solvent. In contrast, when water is added to its THF solution, the emission peaking at 487 nm, gradually intensifies and increases swiftly when f_w is larger than 50% due to the nanoaggregate formation, which is indicative of the AIE feature of **1**.

The changes in the $\Phi_{\rm F}$ values of **1** further verify its AIE activity. Fig. 2B shows a very small $\Phi_{\rm F}$ value (0.33%) in pure THF; however, when water is added, the $\Phi_{\rm F}$ values increase gradually and reach the highest value (18.9%) at the $f_{\rm w}$ of 90%,



Fig. 2 (A) PL spectra of 1 in THF–water mixtures with different volume fractions of water (f_{w}). Concentration: 1×10^{-5} M; excitation wavelength: 360 nm. (B) Fluorescence quantum yield (Φ_F) of 1 versus solvent composition of the THF–water mixture. The Φ_F values were estimated using quinine sulfate in 0.1 M H₂SO₄ (Φ_F = 54.6%) as standard. Inset in panel (B): solutions of 1 in THF and a THF–water mixture with 90% water; photographs taken under illumination of a handheld UV lamp.

which is 57 times higher than that in pure THF. It is amazing that in the thin film state the $\Phi_{\rm F}$ value measured by a calibrated integrating sphere can reach 80.3%, which is 243 times higher than that in the solution state.

Circularly polarized luminescence

Compound 1, possessing both CD and AIE characteristics, is anticipated to possess circularly polarized luminescence (CPL) property. We studied the CPL behavior of 1 in two states: in solution in a good solvent and as a solid thin film by evaporation of its solution on a quartz substrate. An epi-illumination (reflection mode) optical system was home-built to evaluate the CPL activity by recording the differential spontaneous emission, $\Delta I(\lambda) = I_{\rm L}(\lambda) - I_{\rm R}(\lambda)$. This setup is suitable for investigating the chirality of opaque or nontransparent samples with strong light scattering and low transmittance. Fig. 3A reveals the dependencies of ΔI and the emission dissymmetry factor, $g_{\rm em}$, on the wavelength. The sample in the pure solution state was also measured for comparison. No CPL signals were detected in the solution of good solvent because 1 is nonluminescent, and its conformation is randomized by free intramolecular rotation. Once the molecules aggregated as a cast thin film, all ΔI signals become negative with dominant RCP over LCP light emission in the whole monitored spectral region. This demonstrates that the arrangement of luminophores in the aggregates has preferred one-handed helical structures (vide infra). The emission dissymmetry factor, $g_{\rm em}$, is about -0.05 on average in the detected spectral window of 420-620 nm, which is almost the highest value in comparison to the commonly reported conventional pure organic molecules ($\sim 10^{-5}$ to 10^{-2}).¹⁷ In terms of both emission deficiency and dissymmetry factor, the compound presents good results among conjugated organic molecules without introduction of an external chiral field, e.g., a chiralnematic liquid crystalline host, to enhance the helical arrangement of luminophores. Furthermore, the solid sample can preserve the CPL performances even after more than half a year under ambient conditions, which demonstrates that such a characteristic has high stability. This compound is also a promising candidate for fabrication of micrometer- to nanometersized patterns with potential applications such as generation of CPL lasing and information processing and storage.



Fig. 3 Plots of (A) ($l_{\rm L} - l_{\rm R}$) and (B) CPL dissymmetry factor, $g_{\rm em}$, versus wavelength for 1 in THF solution with a concentration of 10⁻⁴ M and drop cast film from 1,2-dichloroethane solution (2 mg mL⁻¹).

Supramolecular assembly

Compound 1 possesses two chiral amino acid attachments, which are anticipated to exert an asymmetric force field on the silole core and induce the formation of helical conformation in the molecule. The CD and CPL spectra have revealed that the helical sense is obvious only when 1 is in a solid state, which is indicative of the formation of characteristic chiral aggregation that forms due to the evaporation of the solvent. Thus, the chiral aggregating behavior of 1 is pivotal for understanding the enhanced helical conformation and chirality-related properties.

We then turned to AFM to investigate the morphological structures of the chiral aggregation of **1**. We first investigated the morphology of the aggregation of **1** on the evaporation of its good solvent, *i.e.*, the THF solution. Helical fibers with consistent left-handedness were formed by **1**, as shown in Fig. 4. The fibers were arranged in an extended way, and thinner fibers were found to helically rotate at different levels to construct thicker ones, which still retained the left-handedness. Because of the hierarchical construction, the helical fibers have a broad distribution of width and helical pitches. This formation of helical fibers corresponds well with the CD spectra in Fig. **1**, suggesting that helical aggregation with a preferred sense has been successfully created by the introduction of chiral attachment to silole.

In addition to evaporation-induced aggregation, aggregates can also be formed by the addition of a poor solvent to the solution of the compound.¹⁸ Thus, we carried out a series of experiments to induce the formation of aggregates by adding different fractions of the poor solvents of compound **1**. We first studied the CD spectra of the mixture by adding increasing amounts of poor solvents, such as water and hexane, to the THF solution. Note that precipitates appeared for the typical concentration of 10⁻⁴ M of **1**, and further dilution could efficiently avoid the formation of the precipitates; however, the



Fig. 4 AFM images of the helical assemblies formed by 1 on the evaporation of its THF solution ($c = 0.001 \text{ mg mL}^{-1}$).

concentration of the diluted solution could not meet the requirement for CD measurement. Therefore, the CD spectrum is not suitable to explore the induced chiral aggregation of the compound due to the poor solvent because of the concentration requirement. Hence, by AFM, we studied the aggregation of 1 on addition of its poor solvent, *i.e.*, water. At a concentration of $\sim 10^{-6}$ M, no precipitate appeared; however, the introduction of the poor solvent, even as small as a 5% fraction of water, caused a dramatic morphological transition, as shown in Fig. 5A and B.

Helical fibers were still formed, but only part of them retained the extended arrangement while the rest associated into loops. Along the circular contour of the loops, braids of helical fibers were clearly observed, indicating that the loops were formed by winding of the helical fibers. The loops were in different dimensions due to the winding of the helical fibers to different extents. Further increase in the water content (to 20%) caused the majority of fibers to wind into loops with only a small fraction retaining the extended arrangement. In fact, the extended fibers still retained left-handedness, but they were much thicker than those that formed with low water content, as shown by the labels in Fig. 5C. The loops were also much thicker and more compact and showed a donut-like shape. When more loops accumulated together, they formed a network, as shown in Fig. 5D. When the water content was as high as 80%, networks of extended fibers were dominant. Moreover, when the water content was as high as 90%, the network of fibers



Fig. 5 AFM images of the helical assemblies formed by 1 on the evaporation of its different THF–water solution. The water content is 5% (A and B), 20% (C and D), 80% (E) and 90% (F).

became much thicker with more fibers joined together, and all the fibres exhibited left-handedness. Thus, we have revealed that 1 formed chiral aggregates on the addition of water. The formation of loops adds additional helical rotation to helical fibers, providing direct evidence that the helical sense is enhanced at different levels in the aggregation process. The clearly observed helical pitches correspond well with the AICD property of the compound as mentioned above. Thus, the aggregation process is pivotal for the transition and amplification of the chirality from the pendant to the silole core. The morphologies of the aggregated structures varied with the conditions under which they were formed. A thorough investigation of the aggregated structures and their corresponding aggregating conditions helps to better understand the critical factors involved in the aggregation.

We further studied the aggregating behavior of 1 on the addition hexane (also a poor solvent for 1), as shown in Fig. 6. When blending with 10% of hexane, the previously formed helical fibers were found to convert into networked structures. When the hexane content further increased to 50%, compound 1 formed braids of fibers arranged in a nebular-like morphology, showing an inclination to wind clockwise. When hexane content increased to 80%, right-handed helical fibers were formed. The helical fibers must have undergone hierarchical assembly because the thick helical fibers were helically twisted by multiple thinner helical fibers and their dimensions were distributed in a wide range. The helical fibers at different assembling levels all showed a consistent right-handedness. Thus, the AFM images clearly showed that the addition of poor solvent such as hexane to the THF solution caused an inversion in the handedness of the helical fibers. The poor solvent effect induced by hexane is different from that induced by water. This difference is expected because water and hexane have opposite polarities. Thus, in a mildly polar solvent like THF, the occurrence of water leads to a gradual increment in the polarity of the solution and finally creates a strong polar environment at higher water contents. The addition of hexane to THF, on the contrary, caused the mixture to undergo a gradual polarity decrease until it finally reached nonpolarity. To balance these diverse external environments, the amphiphilic 1 requires proper adjustment. For instance, the nonpolar silole cores dislike the polar environment, whereas the peripheral amino acids have high affinity with the polar solvent. Therefore, the molecules have to assume an appropriate arrangement that minimizes the contact of silole cores with water and exposes the polar amino acid attachments to the polar environment. In the



Fig. 6 AFM images of the manipulated assemblies formed by 1 on the evaporation of its different THF–hexane mixtures. The hexane content is 10% (A), 50% (B), 80% (C).

nonpolar environment of hexane, however, the silole core and amino acid attachments would assume the opposite arrangement by placing the polar groups inside and leaving the nonpolar silole outside the associated structures. As a consequence of the divergent assembling manners, their assemblies show opposite helical senses.

The addition of poor solvents is the main strategy to induce the AIE property in molecules, and it works well for 1. The AIE effect is usually obvious at very high content of poor solvents (above 70%) in the mixture. Below this percentage, they caused almost no change to the fluorescence emission. The poor solvents exerted their influence by inducing the formation of aggregates, as revealed by particle size analysis, SEM and TEM.¹⁹ A high percentage of poor solvents usually caused the formation of smaller nanoparticles compared with that formed at a low percentage of poor solvents. Because of the simplicity of the aggregates, few reports have focused on the aggregate transformation. By the introduction of amphiphilicity and chirality to the well-known AIE molecule, silole, we have provided a novel AIE system to study the formation of aggregates and their transformation with low to high percentage of solvent. Our AFM images showed that a poor solvent, having fraction as low as 5%, actually led to a dramatic morphological change. They suggested that the addition of poor solvent induced the aggregation of 1 at much lower volume fraction than that detected by fluorescence spectra. The lag in fluorescence detection is due to the different resolutions of AFM and fluorescence spectrometer. AFM reveals the aggregates of molecules on the molecular or supramolecular levels;²⁰ thus, it is more sensitive and able to capture the changes of individual aggregates. However, fluorescence spectrum collects statistical information of the aggregates and is able to show the difference only when the collective contribution of the aggregates is significant enough to reflect their optical properties.

In contrast to the typical silole derivatives, the introduction of chirality to the silole periphery endowed the molecules with the capacity to aggregate into complex architectures. The nanofibers formed by **1**, bearing CD, CPL and AIE properties, have important potential applications in various areas, including electronics and optics. The formation of various aggregates also proves the possibility of fabricating intricate architectures by the incorporation of chirality to the AIE system and manipulating the architectures by changing the content of the poor solvent.

Conclusions

We have synthesized and characterized an amino acid containing silole, which bore both chirality and the AIE properties. The AIE effect boosted the fluorescence quantum efficiency, $\Phi_{\rm F}$, from 0.33% in pure THF to a maximum of 18.9% when water was added, which was 57 times higher than that in pure THF. In the thin film state, the $\Phi_{\rm F}$ value measured by a calibrated integrating sphere can reach 80.3%, which is 243 times higher than that in the solution state. The introduction of chiral valine successfully guided the formation of helical conformation, and the chiral information was further amplified to its higher order assembly as helical aggregates. AFM images show that the compound formed helical fibers on evaporation of its THF solution. On the addition of poor solvent, such as water or hexane (as low as 5%), **1** underwent dramatic morphological transitions accompanied by helical enhancement and inversion in handedness to different extents.

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Notes and references

- 1 Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361.
- 2 S. W. Thomas, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339.
- 3 J. K. An, S. K. Kwon, S. D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, **124**, 14410.
- 4 M. R. Han and M. Hara, New J. Chem., 2006, 30, 223.
- 5 J. D. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, C. Chen, H. S. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740.
- 6 (a) J. Chen, C. C. W. Law, J. W. Y. Lam, S. M. Dong,
 S. M. F. Lo, I. D. Williams, D. Zhu and B. Z. Tang, *Chem. Mater.*, 2003, 15, 15351; (b) Z. Li, Y. Q. Dong, B. Mi,
 Y. Tang, M. Häussler, H. Tong, Y. P. Dong, J. W. Y. Lam,
 Y. Ren, H. H. Y. Sung, K. S. Wong, P. Gao, I. D. Williams,
 H. S. Kwok and B. Z. Tang, *J. Phys. Chem. B*, 2005, 109, 10061.
- 7 (a) X. Zhang, Z. Chi, H. Li, B. Xu, X. Li, W. Zhou, S. Liu,
 Y. Zhang and J. Xu, *Chem. Asian J.*, 2011, 6, 808; (b)
 X. Zhang, Z. Chi, J. Zhang, H. Li, B. Xu, X. Li, S. Liu,
 Y. Zhang and J. Xu, *J. Phys. Chem. B*, 2011, 115, 7606; (c)
 X. Zhang, Z. Chi, H. Li, B. Xu, X. Li, S. Liu, Y. Zhang and
 J. Xu, *J. Mater. Chem.*, 2011, 21, 1788.
- 8 Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332.
- 9 N. Tseng, J. Liu, J. C. Y. Ng, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams and B. Z. Tang, *Chem. Sci.*, 2012, **3**, 493.
- 10 (a) Z. Li, Y. Dong, J. W. Y. Lam, J. Sun, A. Qin, M. Häussler,
 Y. Dong, H. H. Y. Sung, I. D. William, H. S. Kwok and
 B. Z. Tang, *Adv. Funct. Mater.*, 2009, **19**, 905; (b) J. C. Y. Ng,
 J. Liu, H. Su, Y. Hong, H. Li, J. W. Y. Lam, K. S. Wong and
 B. Z. Tang, *J. Mater. Chem. C*, 2014, **2**, 78.
- 11 J. Liu, H. Su, L. Meng, Y. Zhao, C. Deng, J. C. Y. Ng, P. Lu, M. Faisal, J. W. Y. Lam, X. Huang, H. Wu, K. S. Wong and B. Z. Tang, *Chem. Sci.*, 2012, 3, 2737.
- 12 L. M. Lai, J. W. Y. Lam and B. Z. Tang, J. Polym. Sci., Part A: Polym. Chem., 2006, 44, 2117.
- 13 (a) H. Tsumatori, T. Harada, J. Yuasa, Y. Hasegawa and T. Kawai, *Appl. Phys. Express*, 2011, 4, 011601; (b) Y. Shindo and M. Nakagawa, *Appl. Spectrosc.*, 1985, **39**, 32.

- 14 (a) A. Qin, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2010, 39, 2522; (b) H. K. Li, A. J. Qin, J. Z. Sun and B. Z. Tang, *Chin. J. Polym. Sci.*, 2012, 30, 1.
- 15 (a) J. Liu, J. W. Y. Lam and B. Z. Tang, *J. Inorg. Organomet. Polym. Mater.*, 2009, **19**, 249; (b) J. Liu, Y. Zhong,
 J. W. Y. Lam, P. Lu, Y. Hong, Y. Yu, Y. Yue, M. Faisal,
 H. H. Y. Sung, I. D. Williams, K. S. Wong and B. Z. Tang, *Macromolecules*, 2010, **43**, 4921.
- 16 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, 1970.
- 17 (a) T. Kaseyama, S. Furumi, X. Zhang, K. Tanaka and M. Takeuchi, Angew. Chem., Int. Ed., 2011, 50, 3684; (b) J. E. Field, G. Muller, J. P. Riehl and D. Venkataraman, J. Am. Chem. Soc., 2003, 125, 11808; (c) K. E. S. Phillips, T. J. Katz, S. Jockusch, A. J. Lovinger and N. J. Turro, J. Am. Chem. Soc., 2001, 123, 11899; (d) H. Maeda, Y. Bando,

K. Shimomura, I. Yamada, M. Naito, K. Nobusawa, H. Tsumatori and T. Kawai, *J. Am. Chem. Soc.*, 2011, 133, 9266; (e) H. Tsumatori, T. Nakashima and T. Kawai, *Org. Lett.*, 2010, 12, 2362; (f) T. Ikeda, T. Masuda, T. Hirao, J. Yuasa, H. Tsumatori, T. Kawai and T. Haino, *Chem. Commun.*, 2012, 6025.

- 18 G. Yu, Y. Yin, Y. Liu, J. Chen, X. Xu, X. Sun, D. Ma, X. Zhan, Q. Peng, Z. Shuai, B. Z. Tang, D. Zhu, W. Fang and Y. Luo, *J. Am. Chem. Soc.*, 2005, **127**, 6335.
- 19 (a) Y. Dong, J. W. Y. Lam, Z. Li, A. Qin, H. Tong, Y. Dong, X. Feng and B. Z. Tang, *J. Inorg. Organomet. Polym. Mater.*, 2005, **15**, 287; (b) Y. Zhang, J. Xia, X. Feng, B. Tong, J. Shi, J. Zhi, Y. Dong and Y. Wei, *Sens. Actuators*, *B*, 2012, **161**, 587.
- 20 (a) B. S. Li, J. W. Y. Lam, Z. Yu and B. Z. Tang, *Langmuir*, 2012, 28, 5770; (b) B. S. Li, B. Sattin and C. Goh, *Nano Lett.*, 2006, 6, 1474.