

Color Tuning

Highly Solid-State Emissive Pyridinium-Substituted Tetraphenylethylene Salts: Emission Color-Tuning with Counter Anions and Application for Optical Waveguides

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In this paper seven salts of pyridinium-substituted tetraphenylethylene with different anions are reported. They show typical aggregation-induced emission. Crystal structures of three of the salts with $(CF_3SO_2)_2N^-$, $CF_3SO_3^-$, and SbF_6^- as the respective counter anions, are determined. The emission behavior of their amorphous and crystalline solids is investigated. Both amorphous and crystalline solids is are red-emissive. Certain amorphous solids are red-emissive with almost the same quantum yields and fluorescence life-times. However, some crystalline solids are found to show different emission colors varying from green to yellow. Thus, their emission colors can be tuned by the counter anions. Furthermore, certain crystalline solids are highly emissive compared to the respective amorphous solids. Such solid-state emission behavior of these pyridinium-substituted tetraphenylethylene salts is interpreted on the basis of their crystal structures. In addition, optical waveguiding behavior of fabricated microrods is presented.

1. Introduction

Emissive molecules with high quantum yields in the solid states have been intensively explored for applications in organic light emitting diodes (OLEDs),^[1] organic light emitting field transistors,^[2] optical waveguides^[3] and optically pumped lasers.^[4] However, most of luminogens that are highly fluorescent in solutions become weakly or even non-emissive in the aggregation and solid states. Such emission quenching is usually attributed to intermolecular

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small 2014, DOI: 10.1002/smll.201402051



interactions leading to formation of detrimental species such as excimers and exciplexes.^[5] Interestingly, a few organic fluorophores including siloles^[6] and tetraphenylethylenes^[7] show the opposite fluorescent behavior; they are weakly or non-emissive in solution, but they become strongly emissive upon formation of aggregation states and in the solid states.^[8] Such abnormal fluorescent behavior is referred as to aggregation induced (enhanced) emission (AIE), which is ascribed to the inhibition of internal rotations as well as aggregation induced-planarization and formation of J-aggregates in some cases.^[6–9]

AIE fluorophores have received increasing attentions in recent years and sucessfully applied for sensing^[10] and bioimaging.^[11] They have also utilized as light-emitting materials in OLEDs^[12] and optical waveguides.^[13] The results reveal that these AIE luminogens are not only strongly emissive in the solid states, but also responsive to external stimuli such as heating, grinding and chemical vapor.^[13a,14] In fact, organic emissive materials whose emission intensities and colors can be tuned are highly desirable for the practical applications in optoelectronic devices.^[15]



Scheme 1. Synthetic route to compounds 1–7. Reagents and conditions: i) 4-pyridinylboronic acid, Pd(PPh₃)₄, K₂CO₃, THF/H₂O, 75 °C; ii) CH₃I, CH₃CN, 80 °C; iii) AgX, CH₃OH/H₂O, 25 °C.

Tetraphenylethylenes with cationic and anionic moieties were synthesized and investigated mainly for chemosensing^[16] and bio-sensing.^[17] However, their solid state emissions were rarely examined.^[14b,c] In this paper, we report the solid state emission of pyridinium-substituted tetraphenylethylene salts **1–7** (Scheme 1). The results reveal that i) these salts are all red-emissive with relatively high quantum yields (except 1 containing I[–]) in the amorphous states; ii) these salts become more emissive in the respective crystalline states; iii) furthermore, the emission colors are varied from green to yellow by just changing the counter anions; thus, the emission color of the same luminogen (pyridiniumsubstituted tetraphenylethylene) can be tuned by the counter anions. In addition, microrods of **2** and **5** exhibit optical waveguiding behavior with relatively low optical loss coefficients.

2. Results and Discussion

2.1. Synthesis and Crystal Structures

The synthesis of compounds **1–7** is shown in Scheme 1. Suzuki coupling of compound **8** with 4-pyridinylboronic acid led to **9** in 62.2% yield, which was transformed into compound **1** after reaction with iodomethane. Compounds **2–7** were yielded by further reaction of **1** with the respective silver salts in acceptable yields. The chemical structures of **1–7** were confirmed by NMR and MS data and their purities were checked with elemental analysis (see Experimental section).

Crystal structures of 2, 5 and 6 were successfully determined. Figure 1 shows their molecular structures (ORTEP drawings) and intermoleuclar interactions. Their bonding lengths and angles are in normal region. As the carbon atoms C1, C2, C3, C15, C21 and C28 in ethylene moieties are almost coplanar, they were defined as plane A, and the respective four phenyl rings were defined as plane B, C, D and E as shown in Figure 1. The corresponding dihedral angles are listed in **Table 1**. Obviously, subtle differences exist for the conformation of the common luminogen (pyridinium-substituted tetraphenylethylene) in crystals of **2**, **5** and **6**. For instance, the dihedral angles between rings A and D were found to be 64.30° , 45.41° and 45.11° in **2**, **5** and **6**, respectively. Such slight conformation differences can affect the electron conjugation in pyridinium-substituted tetraphenylethylene of **2**, **5** and **6**;^[13a] as a result, crystals of **1–7** are expected to show different absorption and fluorescence spectra (see below).

Figure S1 and Figure 1 show the respective intermolecular arrangements and short interatomic contacts between the pyridinium-substituted tetraphenylethylene cations and counter anions within crystals of 2, 5 and 6. There is no intermolecular face-to-face arrangements among the nighboring pyridinium and phenyl rings, thus no intermolecular pi-pi interactions exist. However, the pyridinium-substituted tetraphenylethylene cations and counter anions are interacted via mutiple short interatomic contacts (see Table S1) within crystals of 2, 5 and 6 as depicted in Figure 1. It is clear that intermolecular orientations of the cations and anions are different witin crystals of 2, 5 and 6; moreover, the cations in 2, 5 and 6 are surrounded and interacted with the respective anions [(CF₃SO₂)₂N⁻, CF₃SO₃⁻, SbF₆⁻] in different ways. This may be regarded as the cations in 2, 5, 6 are influenced by different polar environments.[18]

2.2. Solid-State Emission Behavior

The solutions of **1–7** in good solvents such as CH_2Cl_2 are almost non-emissive (see Figure S2) as reported for other tetraphenylethylene molecules.^[7–14] Also, their solutions show almost the same absorption spectra as depicted in Figure S3, which is consistent with the fact that **1–7** have the common luminogen (pyridinium-substituted tetraphenylethylene). The fluorescence of **1–7** can be switched on after aggregation induced by addition of poor solvent. Figure S2 shows the fluorescence enhancement for solutions of **1–7** in



Figure 1. The ORTEP drawings of 2 (a), 5 (c) and 6 (e); the intermolecular interactions within crystals of 2 (b), 5 (d) and 6 (f).

Table 1. The dihedral angles among rings of A, B, C, D and E within crystals of ${\bf 2,5}$ and ${\bf 6.}$

Compound		Dihedral Angle [°]					
	AB	AC	AD	AE			
2	69.11	55.54	64.30	54.84			
5	52.78	60.25	45.41	57.99			
6	52.67	61.48	45.11	57.62			

CH₂Cl₂ after addition of hexane. Addition of hexane into the CH₂Cl₂ solutions of **1–7** led to the formation of solid precipitates, which were referred as to **1a**, **2a**, **3a**, **4a**, **5a**, **6a** and **7a**, respectively. As depicted in Figure 2a, no XRD signals were detected for **1a-7a**, indicating that they are amorphous. They all are red-emissive with almost the same emission spectra as shown in Figure 3. Their emission quantum yields and lifetimes were measured (see Table 2). Except **1a** with I[–] as the counter anion **2a-7a** exhibit rather similar emission behavior;

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Figure 2. The XRD patterns of 1a-7a (left) and 1b-7b (right).

their quantum yields are varied from 0.37 to 0.45 and emission life-times from 2.75 ns to 3.83 ns. The weak fluorescence of **1a** can be ascribed to the heavy atom effect of iodide anion in **1a**.^[19]

Slow evaporation of the solutions of 1–7 in methanol/ water (1:1, v/v) led to the respective microcrystallines, which were referred as to 1b, 2b, 3b, 4b, 5b, 6b, 7b respectively. The crystallinity of 1b, 2b, 3b, 4b, 5b, 6b and 7b was confirmed by XRD studies. As examples, Figure 4 shows the XRD patterns of 2b, 5b, 6b, which match well with the respective simulated diffraction signals of 2, 5, 6, respectively, based on their single crystal structural data. Thus, it may be concluded that molecular conformations of the cations and the arrangement of the cations and anions within 2b, 5b, 6b are the same as those of single crystals of 2, 5 and 6 (see above), respectively.

The emission behavior of **1b-7b** was investigated. **1b** becomes even weakly emissive because I⁻ may be closer to



Figure 3. a) Photos of samples **1a-7a** under UV light (>365 nm) illumination; b) the fluorescence spectra of **1a-7a**; the excitation wavelength was 410 nm.

the cation luminogen due to the dense packing in the crystalline state than in the amorphous state. However, 2b-7b are more emissive than the respective amorphous solids; as listed in Table 2, the emission quantum yields of 2b-7b are roughly two times of those of 2a-7a, respectively. The average emission life-times of 2b-7b become also longer than those of the respective amorphous solids 2a-7a. Interestingly, these crystalline solids 2b-7b are not red-emissive, and their emission colors are varied from yellow to green (see Figure 5). Their emission spectra are remarkably blue-shifted compared to the corresponding amorphous solids: the emission maxima are shifted in the following order: **2b** ((CF₃SO₂)₂N⁻, 528 nm) < **3b** $(ClO_4^-, 547 \text{ nm}) < 4b (BF_4^-, 548 \text{ nm}) < 5b (CF_3SO_3^-, 557 \text{ nm})$ < 6b (SbF₆⁻, 564 nm) < 7b (PF₆⁻, 574 nm). To the best of our knowledge such anion-dependent emission was rarely reported for organic salts.

It is expected that the cations (pyridinium-substituted tetraphenylethylene) and the respective anions are more densely arranged in the crystalline states than in the amorphous states. As a result, the pyridinium-substituted tetraphenylethylene may adopt a more planar conformation in the amorphous state and become more twisting in the crystalline state. This may interpret the emission blue-shifts of 2b-7b compared to 2a-7a. In fact, the absorption tails above 500 nm of 2a-7a disappear after the transformation into crystalline states (see Figure S4). Moreover, more short intermolecular interactions are anticipated for the crystalline states. For instance, multiple short interatomic contacts are observed within crystals of 2, 5, and 6 as depicted in Figure 1. Accordingly, molecular conformations of the cations will be more fixed in the crystalline states than in the amorphous states, and the internal rotations around sigma bonds within pyridinium-substituted tetraphenylethylene will be inhibited in the crystalline states. Therefore, it is explainable that **2b-7b** are more emissive than **2a-7a**.^[8]

The following two structural facts may interpret that emission colors of 2b-7b are dependent on the respective counter anions: i) crystal structures of 2, 5, and 6 demonstrate that the molecular conformation of the cation luminogen is affected by the intermolecular arrangements that may be influenced by the respective counter anions with different geometrical shapes and sizes. As shown in Table 1, the dihedral angles among phenyl and pyridinium groups

Fable 2.	The photophysical	properties of	famorphous	solids (1a-7a)	and microcrystalline	solids (1b-7b).
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Compounds	Amorphous solids (1a-7a)			Microcrystalline solids (1b-7b)				
	Absorption l _{max} [nm]	Fluorescence l _{max} [nm]	<t>a) [ns]</t>	$\Phi_{\rm f}{}^{\rm b)}$	Absorption l _{max} [nm]	Fluorescence l _{max} [nm]	<τ>a) [ns]	$\Phi_{f}^{b)}$
1	406	614	0.99	0.09	405	-	0.64	0.04
2	408	617	2.75	0.37	410	528	4.03	0.77
3	408	617	3.79	0.41	408	547	5.18	0.89
4	399	616	3.83	0.42	412	548	5.61	0.96
5	405	617	3.69	0.43	412	557	5.87	0.65
6	410	617	3.62	0.37	410	564	4.84	0.87
7	408	617	3.68	0.45	408	574	5.16	0.65

a)An apparent decay time constant < τ > was determined by using the following equation: < τ > = $\frac{\sum_{i=1}^{n} a_i \times \tau_i}{\sum_{i=1}^{n} a_i} (n = 2 - 3)$ where τ_i and a_i , respectively, represent the individual exponential

decay time constant and the corresponding preexponential factor; ^{b)} $\Phi_{\rm f}$ was measured by calibrated integrating sphere.

within crystals 2, 5 and 6 are subtly different, thus the respective cations of 2, 5 and 6 in their crystals adopt different conformations. Thus, the pi-conjugation degree among the pyridinium, phenyl and ethylene moieties within the cation luminogen is subtly different; ii) crystal structures also reveal that the cation luminogens are interacted with the respective anions in different ways. As a result the cation luminogens are affected by different polar environments.

2.3. Tuning the Emission by Exposure to Solvent Vapors and Grinding

It is interesting to note that the amorphous states **2a-7a** and the respective crystalline states **2b-7b** can be inter-converted by exposing to solvent vapors and grinding. Accordingly, the emission colors of these salts can be tuned by exposure to solvent vapors and grinding. As mentioned above the as-prepared amorphous solids are red-emissive. After exposure to vapors of methanol (see Experimental



Figure 4. The XRD patterns of **2b**, **5b** and **6b** and simulated XRD patterns of **2**, **5** and **6** delineated on the basis of their crystal structures using the single crystal software Mercury 1.4.2.

section) all red-emissive solids were transformed into different emission colors ranging from green to yellow (see **Figure 6**a), corresponding well to those of **2b-7b** shown in Figure 5. XRD studies indicate that the solids after treatment with vapors of methanol are crystalline. As an example, Figure 6b shows the XRD pattern of the solid sample which was generated by exposing **2a** to vapors of methanol; diffraction signals at



Figure 5. a) The photos of microcrystalline powders **2b-7b** dispersed in water under UV light (>365 nm) illumination, respectively; b) the normalized fluorescence spectra of **2b-7b** ($\lambda_{max} = 380$ nm) and **2a** ($\lambda_{max} = 410$ nm).

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Figure 6. a) Photos of the amorphous and crystalline samples of 2–7 after exposure to vapors of solvents and grinding taken under light (>365 nm) illumination; b) XRD patterns of 2 after exposure to vapors of solvents and grinding; c) fluorescence spectra of 2 after exposure to vapors of solvents and grinding.

 $2\theta = 6.1^{\circ}$, 12.1°, 20.8° and 24.4° were detected, corresponding well to those of **2b** (see Figure 2b). Thus, vapors can induce the re-crystallization of **2a** and transformation into **2b**. Similarly, it is expected that **3a**, **4a**, **5a**, **6a** and **7a** can be converted into **3b**, **4b**, **5b**, **6b** and **7b**, respectively, after exposure to vapors of methanol.

The crystalline samples **2b**, **3b** and **4b** which were formed by exposure to vapors of methanol became red-emissive again by further exposure to vapors of CH_2Cl_2 as shown in Figure 6a. These solids were found to be amorphous again on the basis of XRD data shown in Figure 6b and Figure S5. But, the crystalline samples of **5b**, **6b** and **7b** could not be transformed into the respective amorphous solids by treatment with vapors of CH_2Cl_2 . However, all crystalline samples **2b-7b** which were generated from the respective amorphous solids after exposure to vapors of methanol could be successfully converted to the amorphous solids again by just grinding the samples (see Figure 6a). These results demonstrate that these crystalline and amorphous solids can be inter-converted by either exposure to vapors of methanol/ CH_2Cl_2 or grinding. As a result, the emission colors of these solids with the common luminogen (pyridinium-substituted tetraphenyleth-ylene) can be tuned.

2.4. Optical Waveguiding Behavior

Microrods of **2b** were successfully yielded by slow evaporation of the MeOH/H₂O (v/v, 1:1) solution, and microrods of **5b** were obtained by slow addition of H₂O into the MeOH solution. **Figures 7**a and 7b show the PL (photoluminescence) images. Clearly, green and yellow-green emissive spots were detected at the respective two rod-ends of microrods of **2b** and **5b**, whereas only rather weaker emission came from the rod-bodies. Thus, microrods of **2b** and **5b** can function as optical waveguides according to previous reports.^[3,13]





Figure 7. a, b) PL microscopy images of microrods of 2b and 5b deposited on glass wafers; c, d) bright-field images (*left*) of 2b and 5b and microarea PL images (*right*) of 2b and 5b by exciting the respective microrods at six different positions with the focused UV laser (380 nm); e, f) spatially resolved PL spectra of the emissions that are out-coupled at the tip of the microrods of 2b and 5b; insets show plots of the peak intensity at the respective maxima vs. the propagation distance for microrods of 2b and 5b.

The respective spatially resolved PL spectra were measured to gain insight into the light waveguiding behaviors within microrods of **2b** and **5b**. As depicted in Figure 7c and 7d micro-area PL spectra were collected at the ends of the respective microrods of **2b** and **5b** under the excitations at different positions (labeled as 1', 2', 3', 4', 5' and 6'). Obviously, the emission intensity at the microrod ends decreases upon increasing the propagation distance. As depicted in the inset of Figure 7e, the emission intensity at 530 nm of the outcoupled light decreases almost exponentially with

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the propagation distance. Note that the emission intensities of the excited points do not change substantially with the position along the microrods. Thus, the inset of Figure 7e can also represent the variation of intensity ratio of incident and outcoupled light vs. the propagation distance. By fitting the data of inset of Figure 7e according to the reported procedure.^[20] the optical loss coefficient at 530 nm for the microrod of **2b** was estimated to be 15.74 dB mm⁻¹. Figure 7f shows the micro-area PL spectra and the variation of the emission intensity vs the propagation distance. Similarly, the optical loss coefficient for the microrod of 5b was estimated to be 14.32 dB mm⁻¹. Based on the fact that the collected PL spectra at the ends of microrods of 2b and 5b under the excitations at different positions are almost the same, selfabsorption may not contribute largely to the optical loss during the light propagation. Thus, it is assumed that the substrate effect and Rayleigh scattering may induce the optical loss observed for microrods of 2b and 5b, according to previous studies.^[21]

It is known that optical waveguides of high performance require emissive molecules with high emission quantum yields in solid states and tunable emission colors. In this aspect, molecules with aggregation-induced emission feature are advantageous in terms of the following considerations: i) they are highly emissive in the solid states, in particular in the crystalline states; ii) their emission wavlengths can be easily tuned by incorproation of appropriate electron donors and acceptors.

3. Conclusion

Seven salts of pyridinium-substituted tetraphenylethylene with different anions were prepared and characterized. The solid state emission behavior of seven salts with the common luminogen (pyridinium-substituted tetraphenylethylene) was discussed. All amorphous solids 2a-7a except the one with I- are red-emissive with almost the same quantum yields and fluorescence life-times. However, the crystalline solids 2b-7b except the one with I⁻ show different emission colors varying from green to yellow. Thus, their emission colors can be tuned by the counter anions. Furthermore, the crystalline solids 2b-7b are highly emissive compared to the respective amorphous solids. On the basis of the crystal structures of 2, 5 and 6 the emission feature of the crystalline solids 2b-7b may be attributed to the following structural characteristics: i) the cation luminogens (pyridinium-substituted tetraphenylethylene) adopt slightly different conformations in the crystals; ii) the cation luminogens are interacted with the respective anions in different ways; iii) multiple interatomic contacts among the cation luminogens and anions will make the conformations of the cation luminogens more rigid and as a result the internal rotations will be inhibited. Finally, microrods of 2b and 5b with green and yellow-green emissions, respectively, exhibit typical optical waveguide behavior. These results clearly demonstrate the promising applications of tetraphenylethylene and its derivatives for highly emissive and color-tunable materials.

4. Experimental Section

Materials and Characterization Techniques: The reagents and starting materials were commercially available and used without any further purification if not specified elsewhere. The water used was purified by Millipore filtration system. Melting points were measured with Büchi B540. ¹H NMR and ¹³C NMR spectra were recorded on Bruker AVANCE III 300 MHz spectrometer and Bruker AVANCE III 400 MHz spectrometer. MS were recorded with BEFLEX III spectrometer. Absorption spectra were recorded on UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu spectrometer). Steadystate fluorescence spectra were recorded with Hitachi (F-4500) spectrophotometers at 25 °C. Fluorescence confocal laser scanning images were recorded with Olympus research inverted system microscope (FV1000-IX81, Tokyo, Japan) equipped with a charge couple device (CCD, Olympus DP71, Tokyo, Japan) camera; the excitation source is a Hg lamp equipped with a band-pass filter (330 ~ 380 nm). All photographs were recorded on a Canon digital camera.

Crystal Structure: Crystals of **2**, **5** and **6** were grown by slow evaporation from the methanol/water solution. All single crystals data were collected on Rigaku Saturn diffractometer with CCD area detector. All calculations were performed using the SHELXL97 and crystal structure crystallographic software packages. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC: 974637, 974638, 974639. X-ray diffraction (XRD) patterns of **1–7** were carried out in the reflection mode at room temperature using a 2 kW Rigaku X-ray diffraction system.

Photophysical Studies: Fluorescence quantum yields of **1–7** in the solids states (amorphous and microcrystalline powders) were recorded on FLSP 920 fluorescence spectroscopy with a calibrated integrating sphere system. Fluorescence lifetimes were measured based on the time-resolved PL experiments which were made with a regenerative amplified Ti: sapphire laser (Spectra-Physics, Spitfi re) at 400 nm (150 fs pulse width, second harmonic). The PL spectra were recorded with a streak camera (C5680, Hamamatsu Photonics) attached to a polychromator (Chromex, Hamamatsu Photonics), for which the temporal and spectral resolutions of the detector are ~ 10 ps and 2 nm, respectively. All the spectroscopic measurements were carried out at room temperature.

Optical Waveguide Measurements: To measure the microarea PL spectra of single microrod, the microrods dispersed on a glass cover-slip were excited with a UV laser (λ = 380 nm, Beamlok, Spectraphysics). The excitation laser was filtered with a band-pass filter (330–380 nm), then focused to excite the microrod with an objective (50x, N.A. = 0.80).

Synthesis and Characterization: Compounds ${\bf 8}$ and ${\bf 9}$ were synthesized according to the reported procedures.^[16a]

Compound **1**: A mixture of compound **9** (1.60 g, 3.41 mmol) and iodomethane(1.45 g, 10.23 mmol) in 30 mL of acetonitrile was refluxed for 5 hours under argon. After cooling to room temperature, the solution was poured into water, extracted with dichloromethane and the organic phase was washed with brine. The organic layer was dried over anhydrous Na_2SO_4 , filtered and evaporated. The residue was subjected to column chromatography with dichloromethane/methanol (v/v, 20/1) as eluent. Compound **1** (1.92 g, 3.14 mmol) was obtained as an orange red solid in 92.2% yield. M.p. 153.2–154.0 °C; ¹H NMR (400 MHz, DMSO- d_6 , δ): 8.94 (d, J = 6.8 Hz, 2H), 8.43 (d, J = 7.0 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.18 (m, 5H), 7.00 (d, J = 6.6 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.72 (m, 4H), 4.29 (s, 3H), 3.68 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, δ): 158.8, 158.6, 155.8, 149.7, 145.5, 143.5, 142.8, 137.5, 135.7, 135.6, 133.0, 132.7, 131.4, 130.6, 128.1, 127.3, 126.7, 124.3, 113.5, 113.2, 55.3, 55.2, 48.6; ESI *m/z*: 484 [M⁺]; Anal. calcd for C₃₄H₃₀INO₂: C 66.78, H 4.94, N 2.29; found: C 66.90, H 5.16, N 2.40.

Compound 2: Silver bis(trifluoromethanesulfonyl)imide (0.15 g, 0.39 mmol) in 3 mL of deionized water was added to a solution of compound 1 (0.2 g, 0.33 mmol) in methanol and the mixture was stirred for 2 hours at room temperature. The solution was poured into water, extracted with dichloromethane and the organic phase was washed with brine. The organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated. Then, compound 2 (0.24 g, 0.31 mmol) was obtained as an orange red solid in 96.2% yield. M.p. 85.5–87.0 °C; ¹H NMR (300 MHz, DMSO- d_6 , δ) 8.94 (d, J = 6.5 Hz, 2H), 8.43 (d, J = 6.5 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 7.18 (m, 5H), 7.00 (d, J = 7.5 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.72 (m, 4H), 4.29 (s, 3H), 3.68 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, δ): 158.8, 158.5, 156.3, 149.8, 144.8, 143.4, 142.8, 137.5, 135.6, 135.5, 133.0, 132.7, 132.6, 131.4, 130.4, 128.1, 127.2, 126.7, 124.4, 121.4, 118.2, 113.4, 113.1, 55.1, 47.6; ESI m/z: 484 [M⁺]; Anal. calcd for C₃₆H₃₀F₆N₂O₆S₂: C 56.54, H 3.95, N 3.66, S 8.39; found: C 56.55, H 4.21, N 3.48, S 8.30.

Compounds **3**, **4**, **5**, **6** and **7** were synthesized and purified similarly as for compound **2** with corresponding silver salts.

Compound **3**: Yield: 98.7%. M.p. 136.0–137.5 °C; ¹H NMR (300 MHz, DMSO- d_6 , δ) 8.94 (d, J = 6.5 Hz, 2H), 8.43 (d, J = 6.5 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 7.18 (m, 5H), 7.00 (d, J = 7.5 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.72 (m, 4H), 4.29 (s, 3H), 3.68 (s, 6H). ¹³C NMR (75 MHz, CDCl₃, δ): 158.7, 158.5, 155.8, 149.6, 145.1, 143.5, 142.6, 137.5, 135.6, 135.5, 132.9, 132.7, 132.6, 131.4, 130.6, 128.1, 127.3, 126.6, 124.3, 113.4, 113.1, 55.2, 55.1, 47.9; ESI *m/z*: 484 [M⁺]; Anal. calcd for C₃₄H₃₀ClNO₆: C 69.92, H 5.18, N 2.40; found: C 69.72, H 2.28, N 5.18.

Compound **4**: Yield: 95.7%. M.p. 128.7–129.2 °C; ¹H NMR (300 MHz, DMSO-*d*₆, δ) 8.94 (d, *J* = 6.5 Hz, 2H), 8.43 (d, *J* = 6.5 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.18 (m, 5H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.72 (m, 4H), 4.29 (s, 3H), 3.68 (s, 6H).¹³C NMR (100 MHz, CDCl₃, δ): 158.8, 158.6, 155.8, 145.2, 142.8, 135.7, 133.0, 132.8, 132.7, 131.5, 128.2, 127.3, 126.8, 124.3, 113.5, 113.2, 55.3, 55.2, 47.8. ESI *m/z*: 484 [M⁺]; Anal. calcd for C₃₄H₃₀BF₄NO₂: C 71.47, H 5.29, N 2.45; found: C 71.02, H 5.15, N 2.37.

Compound **5**: Yield: 94.3%. M.p. 110.4–111.6°C; ¹H NMR (300 MHz, DMSO- d_6 , δ) 8.94 (d, J = 6.5 Hz, 2H), 8.43 (d, J = 6.7 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 7.18 (m, 5H), 7.00 (d, J = 7.1 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.72 (m, 4H), 4.29 (s, 3H), 3.68 (s, 6H). ¹³C NMR (75 MHz, CDCl₃, δ): 158.7, 158.5, 155.9, 149.7, 145.2, 143.4, 142.7, 137.5, 135.6, 135.5, 133.0, 132.7, 132.6, 131.4, 128.1, 127.2, 126.7, 124.3, 113.4, 113.1, 55.2, 55.1, 47.8; ESI m/z: 484 [M⁺]; Anal. calcd for C₃₅H₃₀F₃NO₅ S•0.5CH₃OH: C 65.63, H 4.96, N 2.16, S 4.94; found: C 65.43, H 4.91, N 2.27, S 4.91.

Compound **6**: Yield: 97.4%. M.p. 144.5–145.1 °C; ¹H NMR (300 MHz, DMSO- d_6 , δ) 8.94 (d, J = 6.5 Hz, 2H), 8.43 (d, J = 6.5 Hz,

2H), 7.90 (d, J = 8.4 Hz, 2H), 7.18 (m, 5H), 7.00 (d, J = 7.5 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.72 (m, 4H), 4.29 (s, 3H), 3.68 (s, 6H). ¹³C NMR (75 MHz, DMSO- d_6 , δ): 158.6, 158.4, 153.9, 148.6, 145.9, 143.8, 142.1, 138.0, 135.7, 132.6, 132.5, 131.3, 131.2, 128.6, 128.0, 127.1, 124.0, 113.9, 113.7, 100.0, 55.4, 47.4; ESI m/z: 484 [M⁺]; Anal. calcd for $C_{34}H_{30}F_6NO_2Sb$: C 56.69, H 4.20, N 1.94; found: C, 56.87; H, 4.42; N, 2.11.

Compound **7**: Yield: 96.4%. M.p. 130.4–131.6 °C; ¹H NMR (300 MHz, DMSO- d_6 , δ) 8.94 (d, J = 6.5 Hz, 2H), 8.43 (d, J = 6.5 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 7.18 (m, 5H), 7.00 (d, J = 7.5 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.72 (t, J = 9.4 Hz, 4H), 4.29 (s, 3H), 3.68 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, δ): 158.8, 158.6, 156.0, 149.7, 144.8, 143.5, 142.7, 137.6, 135.7, 135.6, 133.0, 132.7, 131.5, 130.6, 128.1, 127.3, 126.7, 124.3, 113.5, 113.2, 55.2, 47.7; ESI *m/z*: 484 [M⁺]; Anal. calcd for C₃₄H₃₀F₆NO₂P: C 64.86, H 4.80, N 2.22; found: C 64.72, H 4.64, N 2.30.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work is supported by grants from National Natural Science Foundation of China, Ministry of Science and Technology of China and Chinese Academy of Sciences.

- a) T. M. Figueira-Duarte, K. Müllen, *Chem. Rev.* 2011, *111*, 7260;
 b) H. Aziz, Z. D. Popovic, N. X. Hu, A. M. Hor, G. Xu, *Science* 1999, 283, 1900; c) J. Chen, D. Ban, M. G. Helander, Z. H. Lu, P. Poole, *Adv. Mater.* 2010, *22*, 4900; d) S. P. Price, J. Henzie, T. W. Odom, *Small* 2007, *3*, 372.
- [2] a) C. Rost, S. Karg, W. Riess, M. A. Loi, M. Murgia, M. Muccini, *Appl. Phys. Lett.* 2004, *85*, 1613; b) F. Cicoira, C. Santato, *Adv. Funct. Mater.* 2007, *17*, 3421; c) X. Wang, J. Yan, Y. Zhou, J. Pei, *J. Am. Chem. Soc.* 2010, *132*, 15872.
- [3] a) L. M. Tong, R. R. Gattass, J. B. Ashcom, S. L. He, J. Y. Lou, M. Y. Shen, I. Maxwell, E. Mazur, *Nature* 2003, 426, 816;
 b) Q. Liao, H. B. Fu, J. N. Yao, *Adv. Mater.* 2009, 21, 4153;
 c) J. Y. Zheng, Y. L. Yan, X. P. Wang, Y. S. Zhao, J. X. Huang, J. N. Yao, *J. Am. Chem. Soc.* 2012, 134, 2880; d) Y. L. Lei, Q. Liao, H. B. Fu, J. N. Yao, *J. Am. Chem. Soc.* 2010, 132, 1742; e) A. L. Pan, D. Liu, R. B. Liu, F. F. Wang, X. Zhu, B. S. Zou, *Small* 2005, 1, 980; f) C. Shi, Z. Guo, Y. Yan, S. Zhu, Y. Xie, Y. Zhao, W. Zhu, H. Tian, *ACS Appl. Mater. Interfaces* 2013, 5, 192.
- [4] a) X. F. Duan, Y. Huang, R. Agarwal, C. M. Lieber, *Nature* 2003, 421, 241; b) I. D. W. Samuel, G. A. Turnbull, *Chem. Rev.* 2007, 107, 1272; c) Y. S. Zhao, A. D. Peng, H. B. Fu, Y. Ma, J. N. Yao, *Adv. Mater.* 2008, 20, 1661.
- [5] a) J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, **1970**; b) S. A. Jenekhe, J. A. Osaheni, *Science* **1994**, *265*, 765.
- [6] a) X. Y. Qi, H. Li, J. W. Y. Lam, X. T. Yuan, J. Wei, B. Z. Tang, H. Zhang, Adv. Mater. 2012, 24, 4191; b) F. Mahtab, Y. Yu, J. W. Y. Lam, J. Z. Liu, B. Zhang, P. Lu, X. X. Zhang, B. Z. Tang, Adv. Funct. Mater. 2011, 21, 1733; c) G. Yu, S. W. Yin, Y. Q. Liu, J. S. Chen, X. J. Xu,

X. B. Sun, D. G. Ma, X. W. Zhan, Q. Peng, Z. G. Shuai, B. Z. Tang,
D. B. Zhu, W. H. Fang, Y. Luo, *J. Am. Chem. Soc.* 2005, *127*, 6335;
d) J. D. Luo, Z. L. Xie, J. W. Y. Lam, L. Cheng, H. Y. Chen, C. F. Qiu,
H. S. Kwok, X. W. Zhan, Y. Q. Liu, D. B. Zhu, B. Z. Tang, *Chem. Commun.* 2001, 1740.

- [7] a) Q. Chen, D. Q. Zhang, G. X. Zhang, X. Y. Yang, Y. Feng, Q. H. Fan,
 D. B. Zhu, *Adv. Funct. Mater.* 2010, *20*, 3244; b) X. G. Gu, J. J. Yao,
 G. X. Zhang, C. Zhang, Y. L. Yan, Y. S. Zhao, D. Q. Zhang, *Chem. Asian J.* 2013, *8*, 2362; c) G. X. Huang, B. D. Ma, J. M. Chen, Q. Peng,
 G. X. Zhang, Q. H. Fan, D. Q. Zhang, *Chem. Eur. J.* 2012, *18*, 3886.
- [8] a) Y. Hong, J. Lam, B. Z. Tang, *Chem. Soc. Rev.* 2011, 40, 5361;
 b) Y. Hong, J. Lam, B. Z. Tang, *Chem. Commun.* 2009, 43323;
 c) M. Wang, G. Zhang, D. Zhang, D. Zhu, B. Z. Tang, *J. Mater. Chem.* 2010, 20, 1858;
 d) B. An, J. Gierschner, S. Park, *Acc. Chem. Res.* 2012, 45, 544.
- [9] a) Z. Y. Zhang, B. Xu, J. H. Su, L. P. Shen, Y. S. Xie, H. Tian, Angew. Chem. Int. Ed. 2011, 50, 11654; b) B. Wang, Y. C. Wang, J. L. Hua, Y. H. Jiang, J. H. Huang, S. X. Qian, H. Tian, Chem. Eur. J. 2011, 17, 2647; c) P. Kapadia, L. Ditzler, J. Baltrusaitis, D. Swenson, A. Tivanski, F. Pigge, J. Am. Chem. Soc. 2011, 133, 8490; d) X. Gu, J. Yao, G. Zhang, D. Zhang, Small 2012, 8, 3406; e) R. Wei, P. Song, A. Tong, J. Phys. Chem. C 2013, 117, 3467; f) F. Mahtab, J. W. Y. Lam, Y. Yu, J. Z. Liu, W. Z. Yuan, P. Lu, B. Z. Tang, Small 2011, 7, 1448.
- [10] a) M. Wang, D. Zhang, G. Zhang, Y. Tang, S. Wang, D. Zhu, *Anal. Chem.* 2008, *80*, 6443; b) M. Wang, X. Gu, G. Zhang, D. Zhang, D. Zhu, *Anal. Chem.* 2009, *81*, 4444; c) G. Huang, G. Zhang, D. Zhang, *Chem. Commun.* 2012, *48*, 7504; d) Y. Liu, C. Deng, L. Tang, A. Qin, R. Hu, J. Z. Sun, B. Z. Tang, *J. Am. Chem. Soc.* 2011, *133*, 660.
- [11] a) D. Ding, K. Li, B. Liu, B. Tang, Acc. Chem. Res. 2013, 46, 2441;
 b) J. Geng, K. Li, D. Ding, X. Zhang, W. Qin, J. Liu, B. Z. Tang, B. Liu, Small 2012, 8, 3655; c) Y. Huang, F. Hu, R. Zhao, G. Zhang, H. Yang, D. Zhang, Chem. Eur. J. 2014, 20, 158; d) H. Shi, J. Liu, J. Geng, B. Z. Tang, B. Liu, J. Am. Chem. Soc. 2012, 134, 9569;
 e) Y. Yuan, R. Kwok, B. Tang, B. Liu, J. Am. Chem. Soc. 2014, 136, 2546; f) J. Geng, K. Li, W. Qin, L. Ma, G. Gurzadyan, B. Z. Tang, B. Liu, Small 2013, 9, 2012.
- [12] a) W. Yuan, Y. Gong, S. Chen, X. Shen, J. Lam, P. Lu, Y. Lu, Z. Wang, R. Hu, N. Xie, H. Kwok, Y. Zhang, J. Sun, B. Z. Tang, *Chem. Mater.* **2012**, *24*, 1518; b) Z. Guo, W. Zhu, H. Tian, *Chem. Commun.* **2012**, *48*, 6073; c) J. Huang, N. Sun, P. Chen, R. Tang, Q. Li, D. Ma, Z. Li, *Chem. Commun.* **2014**, *50*, 2136; d) J. Huang, N. Sun, Y. Dong, R. Tang, P. Lu, P. Cai, Q. Li, D. Ma, J. Qin, Z. Li, *Adv. Funct. Mater.* **2014**, *23*, 2329; e) J. Huang, R. Tang, T. Zhang, Q. Li, G. Yu, S. Xie, Y. Liu, S. Ye, J. Qin, Z. Li, *Chem. Eur. J.* **2014**, *20*, 5317.

- [13] a) X. Gu, J. Yao, G. Zhang, Y. Yan, C. Zhang, Q. Peng, Q. Liao, Y. Wu,
 Z. Xu, Y. Zhao, H. Fu, D. Zhang, *Adv. Funct. Mater.* 2012, *22*, 4862;
 b) H. Luo, S. Chen, Z. Liu, C. Zhang, Z. Cai, X. Chen, G. Zhang,
 Y. Zhao, S. Decurtins, S. Liu, D. Zhang, *Adv. Funct. Mater.* 2014, *24*, 4250; c) N. Zhao, M. Lin, Y. Yan, J. W. Y. Lam, Y. Zhang, Y. Zhao,
 K. S. Wong, B. Z. Tang, *J. Mater. Chem. C.* 2013, *1*, 4640.
- [14] a) J. Wang, J. Mei, R. Hu, J. Sun, A. Qin, B. Z. Tang, *J. Am. Chem. Soc.* 2012, *134*, 9956; b) N. Zhao, Z. Yang, J. Lam, H. Sung, N. Xie, S. Chen, H. Su, M Gao, I. Williams, K. Wong, B. Z. Tang, *Chem. Commun.* 2012, *48*, 8637; c) Q. Qi, X. Fang, Y. Liu, P. Zhou, Y. Zhang, B. Yang, W. Tian, S. X. Zhang, *RSC Adv.* 2013, *3*, 16986; d) Q. Qi, J. Zhang, B. Xu, B. Li, X. Zhang, W. Tian, *J. Phys. Chem. C* 2013, *117*, 24997.
- [15] a) S. Srinivasan, P. A. Babu, S. Mahesh, A. Ajayaghosh, J. Am. Chem. Soc. 2009, 131, 15122; b) C. Weder, J. Mater. Chem. 2011, 21, 8235; c) X. Y. Shen, Y. J. Wang, E. Zhao, W. Z. Yuan, Y. Liu, P. Lu, A. Qin, Y. Ma, J. Z. Sun, B. Z. Tang, J. Phys. Chem. C 2013, 117, 7334; d) W. Wang, C. Du, C. Wang, M. Hirtz, L. Li, J. Hao, Q. Wu, R. Lu, N. Lu, Y. Wang, H. Fuchs, L. F. Chi, Small 2011, 7, 1403; e) W. Wang, C. Du, H. Bi, Y. Sun, Y. Wang, C. Mauser, E. D. Como, H. Fuchs, L. F. Chi, Adv. Mater. 2010, 22, 2764.
- [16] a) F. Hu, Y. Huang, G. Zhang, R. Zhao, D. Zhang, *Tetrahedron Lett.* **2014**, *55*, 1471; b) Z. Liu, W. Xue, Z. Cai, G. Zhang, D. Zhang, *J. Mater. Chem.* **2011**, *21*, 14487; c) X. Huang, X. Gu, G. Zhang, D. Zhang, *Chem. Commun.* **2012**, *48*, 12915; d) F. Sun, G. Zhang, D. Zhang, L. Xue, H. Jiang, *Org. Lett.* **2011**, *13*, 6378; e) Z. Yang, W. Qin, J. Lam, S. Chen, H. Sung, I. Williams, B. Z. Tang, *Chem. Sci.* **2013**, *4*, 3725.
- [17] a) S. Chen, Y. Hong, Y. Liu, C. Leung, M. Li, R. T. K. Kwok, E. Zhao, J. W. Y. Lam, Y. Yu, B. Tang, J. Am. Chem. Soc. 2013, 135, 4926;
 b) C. Leung, Y. Hong, S. Chen, E. Zhao, J. Lam, B. Tang, J. Am. Chem. Soc. 2013, 135, 62.
- [18] a) P. Magut, S. Das, V. Fernand, J. Losso, K. McDonough, B. Naylor, S. Aggarwal, I. Warner, *J. Am. Chem. Soc.* **2013**, *135*, 15873;
 b) A. Véron, H. Zhang, A. Linden, F. Neüsch, J. Heier, R. Hany, T. Geiger, *Org. Lett.***2014**, *16*, 1044.
- [19] B. Valeur, S. Berberan, N. Mário, *Molecular Fluorescence*, Wiley, Weinheim, **2002**.
- [20] C. Barrelet, A. Greytak, C. Lieber, Nano Lett. 2004, 4, 1981.
- [21] S. Eaton, W. Chen, H. Zhang, R. Iyer, J. Li, M. Ng, S. Ho, J. Aitchison, P. Herman, J. Lightwave Technol. 2009, 27, 1079.

Received: July 12, 2014 Revised: September 10, 2014 Published online: