Design, syntheses and aggregation-induced emission properties of two new enlarged tetraarylethene-based luminogens

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ABSTRACT

Two new enlarged tetraarylethene-based compounds in which biphenyl and 4,5,9,10-tetrahydropyrene cores connect multiple arylethene units have been synthesized through convenient synthetic procedures. The optical properties and electrochemical properties of the two compounds have been investigated. The two compounds possess high emission efficiency in solid state. Particularly, the absolute fluorescence quantum yield of 4,5,9,10-tetrahydropyrene-cored compound in a solid film is up to 44.1%. The emissions of the two compounds in solutions are very weak but they become strong emitters in solid state or in poor solvents, showing aggregation-induced emission (AIE) characteristics. The two compounds exhibit high thermal stability with T_d above 427 °C and show relatively high glass transition temperature with T_g above 142 °C.

Introduction

The design and synthesis of new luminogenic molecules with outstanding properties is one of the most effective approaches to enhance the performance of organic photoelectric devices.[1–5] It is well known that luminogens as the practical materials in organic photoelectric devices should exhibit excellent solid-state fluorescence because they are usually utilized as solid thin film in the devices. Whereas most of the luminogenic molecules, especially those with disk-like shapes, normally suffer from the notorious effect of aggregation-caused quenching (ACQ) in the aggregate state due to the formation of intermolecular π-staking interactions.[6–8] Tang et al. and Park et al. have reported a large number of luminogens which are non-emissive or weak emissive in good solvents but emit intensely in the condensed phase, and this intriguing phenomenon was named as aggregation-induced emission (AIE)[9] or aggregation-induced emission enhancement (AIEE).[10] Thanks to the advantages such as efficient solid-state emission, facile synthesis, and easy functionalization, tetraphenylethene (TPE) as a representative member of AIE dyes has attracted considerable research interest to construct luminogens with efficient solid-state emission.[11–14] Commonly, big molecules with enlarged π-conjugation possess better thermal stability, especially higher glass transition temperatures.[15,16] Therefore, design and synthesis of TPE-based organic molecules with high molecular

mass and enlarged conjugation may be an effective strategy for new AIE materials.

Banerjee et al. have developed an effective synthetic method for tetraarylethenes and a large number of tetraarylethenes with interesting AIE properties have been prepared in good yield by this method.[17–22] During the synthetic procedures of the new tetraarylethenes, the diarylketone intermediates usually play the key roles. However, up to date, the syntheses of ketones for tetraarylethenes are mainly dependent on the Friedel–Crafts acylation reaction of aromatic hydrocarbons with benzoyl chloride and its derivatives. The simple structures of benzoyl chloride and its derivatives decide that they are not good candidates for the synthesis of arylketones which act as the precursors of the arylethenes with high molecular mass and conjugation. Recently, we successfully synthesized biphenyl-based and 4,5,9,10-tetrahydropyrene-based dicarbonyl chloride using a convenient approach, then prepared the enlarged intermediates containing two biarylketone segments based on them and TPE by typical Friedel–Crafts acylation reaction, and finally obtained two big molecules containing multiple arylethene units with enlarged π-conjugation. In addition, the optoelectronic properties of the resultant molecules were investigated in detail.

Results and discussion

The synthetic routes to the two desired compounds are depicted in Scheme 1. In our previous work, we reported that oxalyl chloride can be used to prepare di(polycyclic aryl)ketones by a one-pot reaction with satisfactory result.[23] In this Letter, oxalyl chloride was

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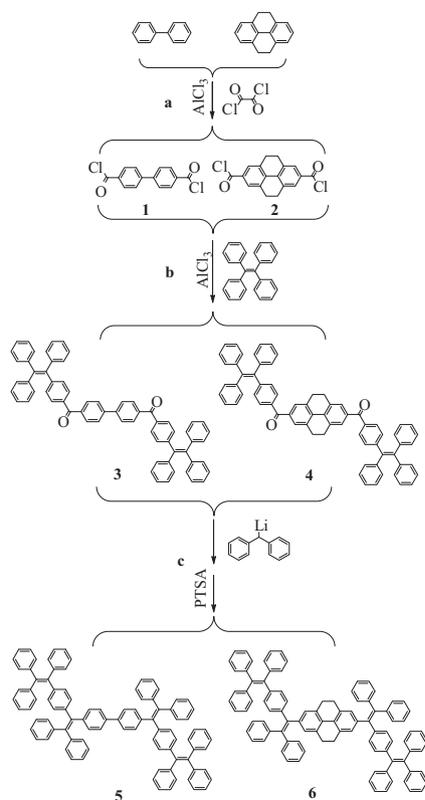
Scheme 1. Synthetic routes to compounds **5** and **6**.

explored to react with biphenyl and 4,5,9,20-tetrahydropyrene to synthesize corresponding dicarbonyl chloride after referring to several relevant papers,[24–26] In this process, the ratio of aromatic hydrocarbons, AlCl₃, and oxalyl chloride were set as 1:3:6, meanwhile, oxygen and water were isolated from the reaction system strictly. In the consideration of the special property of carbonyl chloride, the crude products didn't undergo purification and were employed into the following reactions directly. The key intermediates **3** and **4** were prepared by Friedel–Crafts acylation reaction of **1** and **2** with TPE using AlCl₃ as a catalyst, which were easy to handle. The final total yields of the two steps for the two compounds are 44% and 29%, respectively. The final products **5** and **6** were synthesized via the reaction of compounds **3** and **4** with diphenylmethyllithium at a lower temperature followed by acid catalyzed dehydration of the resulting alcohol in 51% and 58% yields, respectively. The relatively poor solubility of compounds **5** and **6** caused undesired loss in the process of extraction and purification, which is mainly responsible for their only moderate yields.

Figure 1a shows the absorption spectra of compounds **5** and **6**. The ultraviolet (UV) spectra of the two compounds are similar with the absorption maxima at 334 and 343 nm, respectively. The molar absorptivity of compound **5** at 334 nm is $6.92 \times 10^4 \, M^{-1} \, cm^{-1}$, which is lower than that exhibited by compound **6** at 343 nm ($7.52 \times 10^4 \, M^{-1} \, cm^{-1}$). The red-shifted absorption peak and higher molar absorptivity of compound **6** compared with those of compound **5** indicate that compound **6** has higher π-conjugation than that of compound **5**, which is in good agreement with the optical bandgap values estimated from onset of the absorption spectra (Table 1). This can be easily interpreted that the arylethene units connected by 4,5,9,10-tetrahydropyrene in compound **6** tend to arrange into planar structure owing to the smaller dihedral angle of the two phenyl rings in tetrahydropyrene, whereas the arylethene units linked by biphenyl in compound **5** are twisted away from each other, which is detrimental to the electronic communication.

Upon photoexcitation of the dilute solution of the two compounds, the signal in the photoluminescence (PL) spectra are very weak. The absolute fluorescent quantum yields (Φ_F) of their dilute solution were determined using an integrating sphere. The Φ_F value of compound **5** was failed to be obtained due to its weak emission, and the value of compound **6** is 0.16% which is also not very high. According to the intramolecular rotation (IMR) mechanism, the rotation of the phenyl rings effectively deactivates the excited state via a nonradiative decay pathway, and results in the weak emission of the compounds. Although both the compounds are weak emitters in solutions, the samples are highly emissive when they were fabricated into solid films. As shown in Figure 1b, the emission peaks of compounds **5** and **6** are located at 464 and 491 nm, respectively. Their absolute quantum yields measured by using an integrating sphere are 28.8% for compound **5** and 44.1% for compound **6**, which are much higher than the values determined in solutions. The restriction of IMR mechanism can be employed to explain the enormous fluorescence difference between solution state and solid state: the strong intermolecular interactions in solid state can restrict the rotation of the phenyl rings, which blocks the nonradiative channel and enhances the emission. The redder emission wavelength and higher solid-state fluorescent quantum yield of compound **6** than those of compound **5** consist with the absorption behavior of the two compounds, which also can be ascribed to the larger conjugation of compound **6**.

In an effort to further investigate the AIE features of the two compounds, we determined their PL spectra in THF/water mixtures with different water fraction (f_w). As shown in Figure 2a, when the water contents are less than 30%, compound **5** is weakly emissive and the proposed IMR mechanism is responsible for this phenomenon. In mixtures containing 40% water, the PL spectrum begins to appear an emission peak at around 462 nm. The
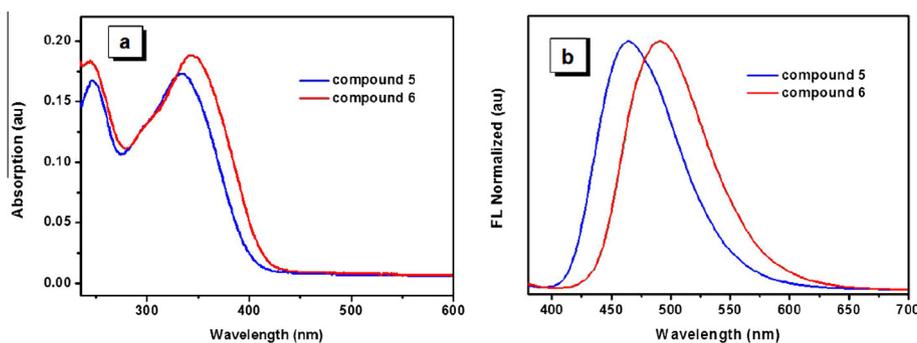
Figure 1. (a) UV–vis spectra of compound **5** and **6** in THF solution. (b) Photoluminescence spectra of compounds **5** and **6** in solid films. Excitation wavelength: 370 nm.

Table 1
Optical and electrochemical properties of compounds **5** and **6**

Compounds	λ_{abs} (nm) Solution[a]	λ_{em} (nm) Film[b]	Φ_F (%) Film	T_g/T_d (°C)	E^{ox}_{onset}	HOMO[c] (eV)	LUMO (eV)	E_g[d] (eV)
5	334	464	28.8	142/485	1.14	−5.46	−2.19	3.27
6	343	491	44.1	152/427	1.03	−5.35	−2.32	3.03

[a] 2×10^{-6} M in THF solution.
[b] Film drop-casted on quartz plate.
[c] HOMO levels were determined using the following equations: HOMO = $-e(E_{onset} - 0.48$ V$) - 4.8$ eV, where the value 0.48 V is for FOC versus SCE electrode.
[d] Estimated from the onset of the absorption spectra: $1240/\lambda_{onset}$.
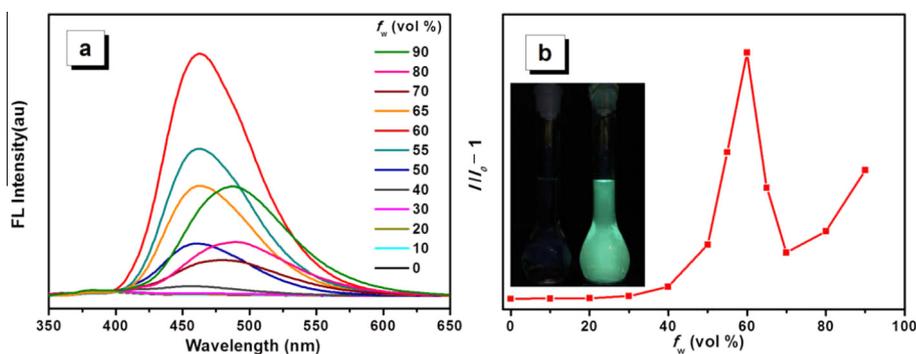
Figure 2. (a) PL spectra of compound **5** in THF/water mixtures with different water fractions (f_w). Inset: photo of compound **5** in THF/water mixtures ($f_w = 0$ and 90%) under UV lamp illumination. Excitation wavelength: 370 nm. (b) Plot of ($I/I_0 - 1$) values versus the compositions of the THF/H$_2$O mixtures of compound **5**, where I_0 is the PL intensity in pure THF solution.

fluorescence intensity of this emission peak increases sharply with increasing the water fractions until the maximum emission intensity is reached in mixtures with 60% water content. A further increase of water leads to a quick decline of the emission intensity. When the water fraction is 70%, the PL intensity decreases to a minimum value and the emission peak is red-shifted with the value of 18 nm. However, after 70% water content, the fluorescence intensities of compound **5** increase again with the increasing water fraction, and the wavelength of 90% fraction is 488 nm. The unusual changes of the PL intensities of compound **5** indicate there is a complicated competition between ACQ and AIE as in Figure 2b. Actually, similar phenomenon was also shown by other compounds,[27,28] but the researchers only speculated the possible reasons.[29–32] To make it clear, transmission electron microscopic (TEM) and dynamic light scattering (DLS) of compound **5** in different water content were measured. In Figure S1, the TEM images show that in 60% THF/water mixture compound **5** is packed in obvious crystalline aggregates and in 80% and 90% water contents, it aggregates into amorphous particles. During the formation process of crystal phase, molecules may adjust their conformation by twisting their phenyl rings to fit into the crystalline lattices.[33] While the molecules in amorphous state aggregate with random style and thus have a more planar conformation. This molecular conformation decides that molecules in amorphous phase are easier to form intermolecular π–π interactions, leading to a red-shifted emission and a decrease of emission compared to those in its crystal state. Hence, during the process of competition between ACQ and AIE, molecular crystal state is more beneficial to AIE than that of amorphous phase. The other important factor which can affect the emission efficiency of the compound is the particle size. Generally, particles with larger size weaken the emission due to that only the molecules on the surface of the nanoparticles can emit fluorescence. The DLS results (Fig. S2) show that the average diameters of 60%, 70%, and 90% water contents of compound **5** are 301, 528 and 374 nm, respectively. Therefore, the quick decrease in emission from 60% to 70% water fractions for

compound **5** is due to the aggregation phase transformation from crystal to amorphous state and the increase in particle sizes. The further emission increase when the water fraction above 70% can be ascribed to the decrease in particle sizes.

The PL spectra of compound **6** in solutions with various water/THF ratios are given in Figure 3a. Similar to common AIE compounds, when the f_w values are small, the emission of the compound is very weak. Along with the increasing water fractions, the emission intensities increase and reach the highest emission efficiency in 90% water content. TEM study of compound **6** in 60%, 70% and 90% water contents (Fig. S3) indicates that only amorphous particles formed. In addition, we measured the average diameter of the particles in 70% and 90% water contents by DLS (Fig. S4). Particles formed in 90% water content have much smaller average diameter (428 nm) than that in 70% water content (606 nm), which is consistent with their emission behavior. It is obvious that the formation of the aggregated state enhances the emission of the compound **6**, showing distinct AIE property.

The thermal properties of compounds **5** and **6** were analyzed by thermo-gravimetric (TGA) and differential scanning calorimetry (DSC) analyses, and are given in Figure S5. Both the compounds show high thermal decomposition (T_d) temperatures with the values of 485 and 427 °C. The thermal stability of **6** is lower than that of compound **5** because the ethylidene in 4,5,9,10-tetrahydropyrene unit is easy to decompose. The (T_g) of Compounds **5** and **6** show relatively high glass transition temperatures with T_g values of 142 and 152 °C, respectively.

The electrochemical properties were investigated by cyclic voltammetry (CV) measurements of the two compounds in anhydrous dichloromethane with the concentration of 1.0×10^{-4} M. The corresponding data are summarized in Table 1. On the basis of the onset potentials of oxidation (E^{ox}_{onset}), the HOMO energy levels were calculated with the values of −5.46 and −5.35 eV using the equation HOMO = $-eE_{onset} - 4.32$ eV. The band gaps were derived from the absorption edge in the absorption spectra with the values of 3.27 eV for **5** and 3.03 eV for **6**. The LUMO values of
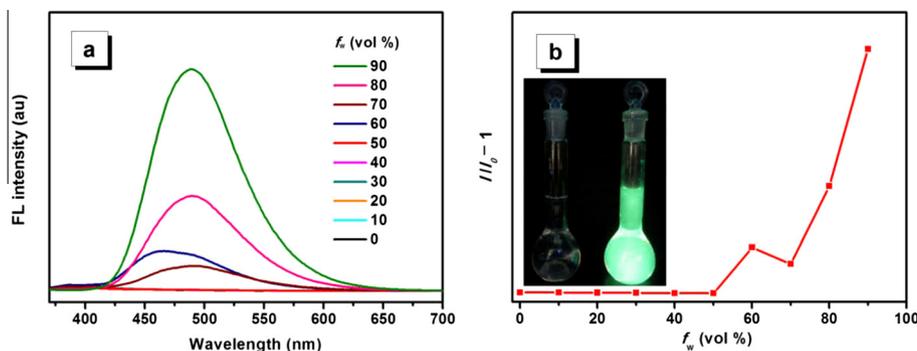
Figure 3. (a) PL spectra of compound **6** in THF/water mixtures with different water fractions (f_w). Inset: photo of compound **6** in THF/water mixtures (f_w = 0 and 90%) under UV lamp illumination. Excitation wavelength: 370 nm. (b) Plot of ($I/I_0 - 1$) values versus the compositions of the THF/H_2O mixtures of compound **6**, where I_0 is the PL intensity in pure THF solution.

samples can be estimated by subtraction of the optical band gap energies from the HOMO energy levels with the values of −2.19 eV for **5** and −2.32 eV for **6**. These data further demonstrates that compound **6** processes larger π-conjugation in comparison with that of compound **5**.

In summary, based on biphenyl and 4,5,9,10-tetrahydropyrene, compounds **5** and **6** which bear multiple arylethene units and possess expanded π-conjugation have been synthesized. A convenient preparation method for the key intermediates aryl-based dicarbonyl chlorides for new tetraarylethenes has been developed. In contrast with compound **5**, compound **6** shows longer absorption and emission wavelengths and narrower optical bandgap, meanwhile, it also has a higher HOMO value. The two compounds exhibit a high thermal stability and a relatively high glass transition temperature. Both the compounds show AIE properties and have high solid-state fluorescence quantum yields, especially compound **6** with the value of 44.1%. This work provides an effective strategy for enlarged tetraarylethene-based AIE materials, further systemic work focusing on the design, synthesis, photoelectric properties and OLED application of new AIE compounds are under investigation in our lab.

Acknowledgements

Supplementary data

Supplementary data (these data include experimental details, TEM and DLS results and thermal properties of the two compounds described in this Letter) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.03.071.

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