ChemComm

Chemical Communications

www.rsc.org/chemcomm
Volume 49 | Number 25 | 28 March 2013 | Pages 2465–2580

ISSN 1359-7345

RSC Publishing

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Zujin Zhao, Ben Zhong Tang *et al.*
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From tetraphenylethene to tetranaphthylethene: structural evolution in AIE luminogen continues†

Jian Zhou,[a] Zhengfeng Chang,[a] Yibin Jiang,[b] Bairong He,[a] Man Du,[a] Ping Lu,[c] Yuning Hong,[d] Hoi Sing Kwok,[b] Anjun Qin,[e] Huayu Qiu,[a] Zujin Zhao*[a] and Ben Zhong Tang*[d]

Cite this: *Chem. Commun.*, 2013, **49**, 2491

Received 1st January 2013,
Accepted 28th January 2013

DOI: 10.1039/c3cc00010a

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Replacement of phenyl ring(s) in tetraphenylethene by naphthalene ring(s) generates a series of new luminogens with aggregation-induced emission (AIE) characteristics, demonstrating that bulky naphthalene rings can serve as a rotor to construct AIE luminogens.

Aggregation-induced emission (AIE),[1] a novel phenomenon opposite to commonly observed aggregation-caused quenching (ACQ), is attracting intense research interest due to its significant academic value and diverse promising applications in fluorescent sensors,[2] bioprobes,[3] optoelectronic devices,[4] mechanochromic smart materials,[5] *etc.* Great endeavors have been devoted to fundamental understanding of the mechanism behind the AIE phenomenon, both to solve ACQ and to develop efficient solid-state light emitters. Numerous evidences from theoretical calculations and experimental results have rationalized that restriction of intramolecular rotation (IMR) is the main cause for the AIE effect.[6,7] The rotation of aromatic rotors, that annihilate the excitons in a nonradiative fashion in the solution state, is restricted in the aggregated state and thus the radiative decay of the excited state becomes dominant, rendering the luminogens emissive. Therefore, aromatic rotors are important in the design of AIE luminogens. The mostly used rotors are phenyl rings, while other bulky planar aromatic rings are rarely adopted as rotors in AIE luminogens. The difficulty may lie in the connection patterns between rotors and stators. When the aromatic rotors become coplanar with the stators, both segments are conjugated effectively. Such planar π-conjugated luminogens show moderate emission efficiency due to the good conjugation and synergistic effect between the rotors and stators, even if the motion of the aromatic rotors indeed quenches the light emission to a certain extent.[8] This may be one of the reasons why the AIE effect is not observed for most π-conjugated planar chromophores. To gain a deeper insight into the creation of AIE luminogens, we cast our attention on tetraphenylethene (TPE),[4a,6d,9] a splendid AIE luminogen with a twisted, propeller-like conformation. We wondered whether AIE luminogens are accessible when bulky aromatic rotors take the place of phenyl rings. Herein, a series of tailored naphthalene-substituted ethenes (Chart 1) were prepared and their photoluminescence (PL) and electroluminescence (EL) properties compared with those of the TPE parent.

The naphthalene-substituted ethenes were synthesized *via* homo- or cross-couplings of diphenyl ketone, 2-naphthyl phenyl ketone and 2,2′-dinaphthyl ketone in the presence of $TiCl_4$ and zinc dust (Scheme S1†). The detailed procedures and characterization data are given in ESI†. All the luminogens are soluble in common organic solvents such as dichloromethane and tetrahydrofuran (THF) but are insoluble in water. Theoretical calculations disclose that they possess a highly twisted

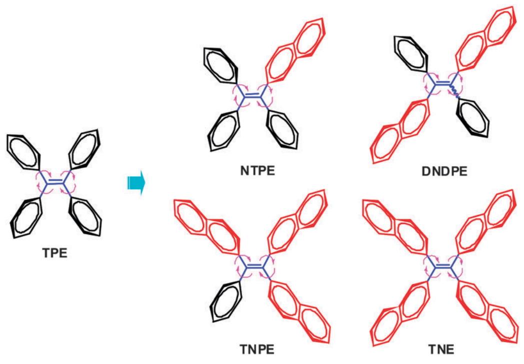

Chart 1 Molecular structures of naphthalene-substituted ethenes.

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[a] College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, China. E-mail: zujinzhao@gmail.com

[b] Center for Display Research, The Hong Kong University of Science & Technology, Kowloon, Hong Kong, China

[c] State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, China

[d] Department of Chemistry, Institute of Molecular Functional Materials, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China. E-mail: tangbenz@ust.hk

[e] Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

† Electronic supplementary information (ESI) available: Experimental, optimized molecular structures and calculated HOMO and LUMO energy levels, TGA and DSC curves, absorption spectra, VT ^1H NMR spectra of TNE, PL spectra and characteristic curves of EL device, see DOI: 10.1039/c3cc00010a

Table 1 Optical and thermal properties of naphthalene-substituted ethenes[a]

	λ_{abs}/nm	λ_{em}/nm		Φ_F (%)			T_g/T_d
	Soln	Soln[a]	Film[b]	Soln[c]	Film[d]	α_{AIE}[e]	(°C)
TPE	299	—	475	0.24	49.2	205	—/224
NTPE	324	392	487	0.81	45.0	56	53/236
DNDPE	333	393	491	1.09	30.1	28	56/270
TNPE	341	393	493	1.64	37.4	23	95/314
TNE	349	394	494	1.66	22.4	13	—/348

[a] In THF solution (10 μM). [b] Film drop-casted on quartz plate. [c] Determined in THF solution using 9,10-diphenylanthracene (Φ_F = 90% in cyclohexane) as standard. [d] Determined in amorphous film by integrating sphere. [e] $\alpha_{AIE} = \Phi_{F,A}/\Phi_{F,S}$.

conformation (Fig. S1†), which leads to little orbital overlapping and poor electronic communication between the aromatic rings. The thermal stability of the luminogens is increased on replacement of phenyl by naphthyl, as indicated by enhanced decomposition temperatures (T_d) from TPE (224 °C) to TNE (348 °C) (Fig. S2†); TNPE shows a highest glass-transition temperature (T_g) of 95 °C (Table 1).

The absorption spectra of the luminogens in THF solutions are red-shifted with increasing naphthalene ring substitution (Fig. S3†), which is in good agreement with the calculation results of progressively narrowed energy bandgaps (Fig. S4†). Replacement of a phenyl with a naphthalene ring results in a bathochromic shift of ~9 nm in the absorption spectra of naphthalene-substituted ethenes. TNE shows its absorption maximum at 349 nm, bathochromically shifted by 50 nm in comparison with that of TPE. Whereas TPE emits almost no light in the solution state, weak fluorescence peaks at 392–394 nm are recorded from solutions of naphthalene-substituted ethenes. The fluorescence quantum yields in solutions ($\Phi_{F,S}$) of these luminogens are in the range of 0.81–1.66%, which are enhanced slightly with increase of naphthalene rings. The $\Phi_{F,S}$ values are higher than that of TPE (0.24%) but much lower than that of naphthalene itself (23%),[10] which is consistent with our previous findings.[11] The IMR process of naphthalene ring(s) against the olefin stator that is active in the solution state can consume the excited-state energy of the luminogens, rendering the luminogens weakly fluorescent. Meanwhile, the IMR process also undermines the electronic communication between the naphthalene and/or phenyl rings and thus results in an ineffective conjugation. Therefore, the short-wavelength emission should be due to the naphthalene moieties of limited extension rather than the whole molecule. On the other hand, since naphthalene is more bulky than phenyl, the stiffness of the luminogen is reinforced slightly with increase of naphthalene substitution. In addition, the naphthalene ring is more fluorescent than the phenyl ring.[10] Both effects work collectively making the naphthalene-substituted ethenes fluoresce more efficiently than TPE in solution.

Variable-temperature (VT) ^{1}H NMR study reveals that the sharp NMR resonance peaks of TNE become broad and structureless when the temperature is lowered (Fig. S5†), due to the restriction of the IMR process that causes fast conformational exchanges, and hence sharp NMR resonance peaks. The changes in ^{1}H NMR spectral profiles of TNE are more significant than those of TPE at low temperatures,[12] demonstrating that the motions of the bulky naphthalene rotors are constrained more readily than for phenyl.

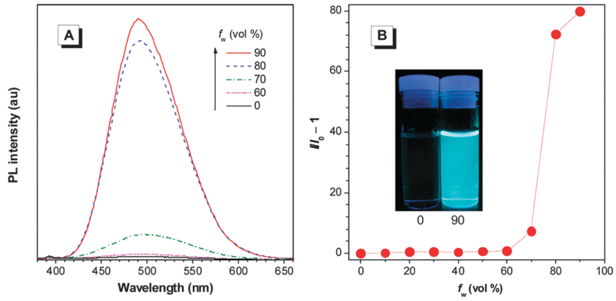

Fig. 1 (A) PL spectra of TNE in THF–water mixtures with different water fraction (f_w). (B) Plots of $(I/I_0) - 1$ *vs.* f_w, where I_0 is the PL intensity in pure THF solution. Inset: photos of TNE in THF–water mixtures (f_w = 0 and 90%) under UV lamp illumination.

To check whether the naphthalene-substituted ethenes are AIE active water was added into their THF solutions and the PL spectra in THF–water mixtures recorded. Fig. 1 illustrates the PL spectra of TNE as an example. When the water fraction (f_w, vol%) in the THF–water mixture is low ($f_w \leq 60\%$), the PL emission remains very weak and varies only slightly. When a large amount of water is added ($f_w \geq 70\%$), a long-wavelength emission with a peak at 492 nm appears with greatly enhanced intensity. Since TNE is insoluble in water, increase of water content causes TNE molecules to aggregate. The aggregate formation deactivates the IMR process and thus populates the radiative decay of the excitons, making the luminogen fluoresce strongly. Meanwhile, the conjugation is improved by restriction of the IMR process, and thereby the long-wavelength emission originating from the whole molecule becomes dominant. Similar emission behaviors are observed for NTPE, DNDPE and TNPE in THF–water mixtures (Fig. S6†), verifying that these luminogens are AIE-active.

The naphthalene-substituted ethenes are also emissive in the solid state. Their films show intense PL emissions with peaks in the range of 487–494 nm (Fig. 2A). The fluorescence quantum yields in the aggregate state ($\Phi_{F,A}$) of TPNE, DNDPE, TNPE and TNE are 45.0, 30.1, 37.4 and 22.4%, respectively, which are much higher than those in solutions, but are lower than that of TPE (49.2%). The AIE effect is weakened as phenyl is replaced by naphthalene, as evidenced by the decreased α_{AIE} values from 205 of TPE to 13 of TNE (Table 1). The planar naphthalene ring is about twice the size of phenyl and this makes it much easier to form π-stacking between naphthalene rings.

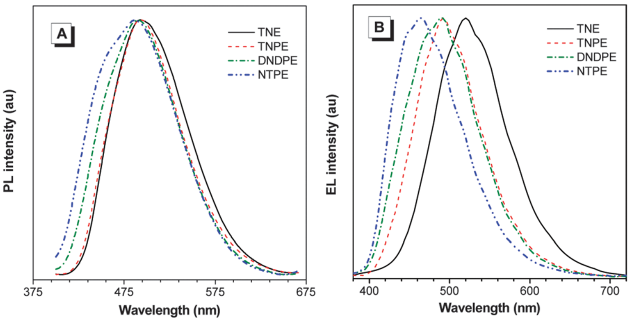

Fig. 2 (A) PL and (B) EL spectra of thin neat films of naphthalene-substituted ethenes.

Table 2 EL properties of naphthalene-substituted ethenes[a]

	EL/nm	V_{on}/V	$L_{\max}$/ cd m^{-2}	$\eta_{\mathrm{P,max}}$/ lm W^{-1}	$\eta_{\mathrm{C,max}}$/ cd A^{-1}	$\eta_{\mathrm{ext,max}}$ (%)
TPE[b]	445	2.9	1800	0.35	0.45	0.4
NTPE	464	5.6	4130	0.5	1.0	0.6
DNDPE	488	5.6	5900	0.7	1.4	0.7
TNPE	492	4.2	12300	2.0	3.0	1.2
TNE	520	5.2	8840	1.6	2.9	1.0

[a] Abbreviations: V_{on} = turn-on voltage at 1 cd m^{-2}, $L_{\max}$ = maximum luminance, $\eta_{\mathrm{P,max}}$, $\eta_{\mathrm{C,max}}$ and $\eta_{\mathrm{ext,max}}$ = maximum power, current and external quantum efficiencies, respectively. [b] Ref. 9*b*.

The naphthalene rings of adjacent TNE molecules can partially overlap each other in the solid state, leading to strong intermolecular interactions and decreased emission efficiency.

To evaluate the EL property of naphthalene-substituted ethenes, multilayer OLEDs with a configuration of ITO|NPB (60 nm)|emitter (20 nm)|TPBI (40 nm)|LiF (1 nm)|Al (100 nm) were fabricated, where the new luminogens functioned as emitters, and *N*,*N*-bis(1-naphthyl)-*N*,*N*-diphenylbenzidine (NPB) and 2,2′,2″-(1,3,5-benzinetriyl)tris(1-phenyl-1-*H*-benzimidazole) (TPBI) served as hole- and electron-transporting layers, repectively. The device performances are summarized in Table 2. The EL emissions of the luminogens move to longer wavelength with increase of naphthalene rings (Fig. 2B) and the emission color become much redder than that of TPE (445 nm). NTPE shows EL emission at 464 nm, which is blue-shifted by 23 nm than that of its amorphous film, probably due to the crystalline nature of the vacuum-deposited film in the device. The EL emissions of DNDPE (488 nm) and TNPE (492 nm) are close to the PL emissions of their films, while that of TNE is bathochromically shifted to 520 nm due to the microcavity effect. The device performances of naphthalene-substituted ethenes are superior to that of TPE (Fig. S7†). The device of TNPE shows the best EL performances. It is turned on at 4.2 V and radiates strongly with a maximum luminance of 12 300 cd cm^{-2} at 15 V. The maximum current and external quantum efficiencies attained by the device are 3.0 cd A^{-1} and 1.2%, respectively, which are improved remarkably in comparison with those obtained from the device of TPE (1800 cd m^{-2}, 0.45 cd A^{-1} and 0.4%),[9b] probably due to the better carrier transport relative to TPE.

In summary, a series of AIE-active naphthalene-substituted ethenes are synthesized and characterized. They are weakly fluorescent in the solution state because the rotation of naphthalene rotors against the olefin stator quenches the light emission. However, they are induced to fluoresce efficiently in the aggregate state, where the nonradiative decay pathway is blocked. Although the AIE effect is weakened with the accumulation of naphthalene rotors, the luminogens are compensated with improved thermal and EL properties. The results obtained in this work demonstrate that bulky aromatic rings can be used as rotors in the construction of AIE luminogens with tailored propeller-like architecture.

We acknowledge the financial support from the National Natural Science Foundation of China (51273053, 21104012 and 21074028), the National Basic Research Program of China (973 Program, 2013CB834702), the Program for Changjiang Scholars and Innovative Research Teams in Chinese Universities (IRT 1231) and the Project of Zhejiang Key Scientific and Technological Innovation Team (2010R50017). B. Z. Tang thanks the support of the Guangdong Innovative Research Team Program of China (20110C0105067115).

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