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Received 14th August 2014 Accepted 12th November 2014 Electron donating group stimulated aggregation induced emission enhancement of oligophenylenevinylene-cored luminogens†

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Three new oligophenylenevinylene (OligoPV)-cored luminogens were synthesized by utilizing the Suzuki coupling/Buchwald-Hartwig amination reaction and their aggregation-induced emission properties have been studied. Out of three, two are aggregation-induced emission enhancement (AIEE)-active molecules: weakly fluorescent in solution, while highly emissive in the aggregation state. The presence of the OligoPV core has turned an aggregation-caused quenching (ACQ) luminophore into an AIEE one. They show excellent solubility in common organic solvents, emit light in the green region (500–516 nm) and have high thermal stability.

Fluorescent molecular materials have been intensively studied as active materials for organic light-emitting diodes (OLEDs), lasers, and sensor applications.^{1,2} Many of the fluorescent molecules have efficient emission in solution, however, the emission tends to vanish in the solid-state due to aggregationcaused quenching (ACQ).³ The best approach to this notorious problem is to develop new luminophoric materials whose aggregates can emit more efficiently than their solutions. Along this line of approach, two novel photoluminescence (PL) processes have been identified: one is the "aggregation-induced emission enhancement (AIEE)"4 and another is the "aggregation-induced emission (AIE)".5,6 These phenomenon are mainly ascribed to the restriction of intramolecular rotations (RIR) process. For example, the nonluminescence of silole in solution is attributed to the active intramolecular rotations of multiple phenyl rings on its periphery, while the strong emission in the solid state is caused by the restriction of intramolecular rotations of those phenyl rings. This intriguing finding paves a new avenue to tackle the notorious aggregationcaused quenching (ACQ) of conventional chromophores. Now, researchers have greatly expanded their search for AIEE luminogens that show specific applications in materials science7 and biological technology.8 For example, tetraphenylethene (TPE) is a representative AIEE-active luminophore and TPE-derivatives have been widely used as fluorescent probes for the detection of ions, biomolecules and explosives.9 Recently, Tang et al. shown that tetraphenylethene (TPE) could be used as a modifier to turn an ACQ luminophore to an AIEE one.4,10 These successes triggered our interest to conjecture whether oligophenylenevinylen (OligoPV) free of ACQ effect and promising emitters for organic light-emitting diodes (OLEDs)? Are they serves as a core and conventional chromophores as peripheries? To answer these questions, herein, we elaborate three luminogens by decorating a p-phenylenevinylene core with four electron donating ACQ luminophores [triphenylamine (TPA), thiophene (T) and carbazole (C)] at para positions. Generally electron donating groups have quite a different effect on π -delocalization of conjugate systems, especially when attached at the para position giving a highest fluorescence quantum yield compared to ortho- and meta-substitution.11

Oligophenylenevinylene (OligoPV) based core unit is accessible from the general synthesis route given in Scheme 1, with the key building blocks being a diphosphonate 3 and 4,4'-dibromobenzophenone. 1,4-Bisdodecyloxybenzene $(1)^{12}$ was bisbromomethylated in glacial acetic acid solution with paraformaldehyde and hydrogen bromide to yield dibromo derivative 2.¹³ This dibromide 2 is then treated with triethyl phosphite in an Arbuzov reaction to give diphosphonate 3. A Horner-Wadsworth–Emmons (HWE) reaction between diphosphonate 3 and 4,4'-dibromobenzophenone yields the OligoPV based core unit 4 (OligoPV-4Br).

Final construction of the targeted molecule is illustrated in Scheme 2. To achieve the synthesis of these oligomers Suzukitype coupling reactions have been explored. The synthesis of the tetra-substituted OligoPVs 5/6 was achieved by using Suzukitype cross-coupling reaction between 2-thienylboronic acid/4-(diphenylamino)phenylboronic acid and bromo derivative 4.

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Scheme 2 Reagents and conditions: (a) 2-thienylboronic acid, Pd(PPh₃)₄, K₂CO₃, toluene, H₂O, aliquat 336, 90 °C, 16 h; (b) 4-(diphenylamino) phenylboronic acid, Pd(PPh₃)₄, K₂CO₃, toluene, H₂O, aliquat 336, 90 °C, 16 h; (c) carbazole, Pd(OAc)₂, P(t-Bu)₃, NaOt-Bu, toluene, 100 °C, 3 days.

Products OligoPV–T 5 and OligoPV–TPA 6 were obtained in good yields ranging from 74% to 71%. OligoPV–C 7 was obtained from tetrabrominated OligoPV based core 4 with carbazole¹⁴ *via* fourfold Pd-catalyzed Buchwald-Hartwig amination in 49% yield. These oligomers are readily soluble in common organic solvents, such as CHCl₃, CH₂Cl₂, THF and toluene but insoluble in methanol and water. They were purified conveniently by column chromatography rather than vacuum sublimation usually used for the purification of insoluble organic semiconductors. ¹H and ¹³C NMR spectra and MALDI-TOF MS associated with elemental analysis were employed to confirm the structure and purity of all new compounds.

We measured the UV/Vis absorption and fluorescence spectroscopic data of these synthesized compounds in toluene and tetrahydrofuran solutions and the results are presented in Table 1. The UV/Vis absorption spectra of the luminogens in THF are shown in Fig. 1a. The absorption spectra of three compounds have two absorption bands in the 312–360 nm and 388–420 nm regions. The first absorption band in the short wavelength region around 312–360 nm was attributed to the central phenylenevinylene segment based on the presence of absorption band at 343 nm for compound 4 in THF. The second absorption band at 388–420 nm is due to π – π * transition from between central phenylenevinylene unit and peripheral electron donating unit. Particularly for compound OligoPV–TPA, the first

Table 1 Photophysical properties of derivatives OligoPV-TPA, OligoPV-C and OligoPV-T												
Compound	UV-vis (λ_{abs} , nm)		$\frac{\varepsilon_{\max}^{a}}{(10^4 \mathrm{mol}^{-1} \mathrm{cm}^{-1})}$		PL $(\lambda_{\max}, \operatorname{nm}, \varphi_{\operatorname{fl}}^{b})$			Stokes shifts ^{c} (10 ³ cm ⁻¹)		ΔE^d (eV)		
	Tol	THF	Tol	THF	Tol	THF	Solid	Tol	THF	Tol	THF	$T_{\rm d}$ (°C)
OligoPV–TPA OligoPV–C OligoPV–T	356, 418 320, 411 307, 388	360, 420 324, 413 312, 388	9.16 6.84 6.15	$8.12 \\ 5.46 \\ 5.16$	510(0.194) 500(0.230) 509(0.221)	515(0.186) 504(0.225) 516(0.213)	516 534 526	0.85 1.10 0.61	0.84 1.12 0.64	3.48 3.87 3.19	3.44 3.82 3.19	340 390 352

 $^{a} \varepsilon_{\text{max}}$ is the extinction coefficient at λ_{max} of absorption. b Fluorescence quantum yields, measured in solution using Rhodamine B ($\Phi_{\text{fl}} = 0.43$, in acidic methanol) as standard, excited at 551 nm. c Stokes shift = ($1/\lambda_{\text{abs}} - 1/\lambda_{\text{em}}$). d Determined from UV-vis absorption maximum.



Fig. 1 (a) Absorption spectra of OligoPV-cored luminogens ($C = 1 \times 10^{-6}$ M) in THF. (b) Photoluminescence spectra of OligoPV-cored luminogens ($C = 1 \times 10^{-7}$ M) in THF. Inset: fluorescence emission image in THF. (c) Corresponding emission spectra of compound OligoPV-TPA in aqueous THF with different water-THF ratios at 10^{-7} M. Inset: fluorescence emission image of OligoPV-TPA ($f_w = 0$, 50 and 90%). (d) Changes of peak intensity with water fraction of compound OligoPV-TPA. (e) Corresponding emission spectra of compound OligoPV-T in aqueous THF with different water-THF ratios at 10^{-7} M. Inset: fluorescence emission image of OligoPV-TPA ($f_w = 0$, 50 and 90%). (d) Changes of peak intensity with water fraction of compound OligoPV-TPA. (e) Corresponding emission spectra of compound OligoPV-T in aqueous THF with different water-THF ratios at 10^{-7} M. Inset: fluorescence emission image of OligoPV-T ($f_w = 0$, 50 and 90%). (f) Normalized fluorescence (FL) spectra in powdered state. Inset: photographs in powder form. All photos are taken under UV illumination. Excitation wavelength: 365 nm.

absorption peak (360 nm) is slightly red shifted compare to that of OligoPV-C (324 nm) and OligoPV-T (312 nm). The red shift we ascribe to the increased π -electron density on the central phenylenevinylene segment, arising from the electron-donating nature of the triphenylamine moiety. Optical absorption spectrum of OligoPV-C was slightly red shifted by *ca.* 12 nm in comparison to OligoPV-T which could be attributed to the carbazole group having the high electron-donating ability compare to the thiophene group. The fluorescence emission bands of OligoPV-TPA, OligoPV-C and OligoPV-T were almost identical (Fig. 1b), only one emission band was observed in the green region. The fluorescence spectrum of OligoPV-TPA (exited at 360 nm) in THF showed a sharp emission band at 515 nm. Similarly, the fluorescence spectrum of OligoPV-C (excited at 324 nm) and OligoPV–T (excited at 388 nm) in THF resulted in an emission at 504 nm and 516 nm respectively. All absorption and emission spectra are blue-shifted in less polar solvent (toluene) compare to THF. The emission peak of OligoPV–TPA was blue shifted about 5 nm in toluene than that of THF, which showed that there was an obvious much more π – π * delocalization with the introduction of the triphenylamine moiety. Same type of blue shift was also observed in OligoPV–C (4 nm) and OligoPV–T (7 nm). The high molar extinction coefficient values of these compounds OligoPV–TPA, OligoPV–C and OligoPV–T (51 600–91 696 L mol⁻¹ cm⁻¹) compared to TPA, C and T (12–3493 L mol⁻¹ cm⁻¹) can be reasoned as a combined effect of high molecular weights and of the presence of multi conjugated OligoPV–core in each molecule. The Stokes' shifts of

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OligoPV-TPA, OligoPV-C, and OligoPV-T were calculated to be 0.84, 1.12, and 0.64 nm in THF and 0.85, 1.10, and 0.61 nm in toluene respectively (Table 1). The negligible Stokes' shifts indicate that the intramolecular charge transfer (ICT) properties for these luminogens are very weak. The fluorescence quantum yields $(\Phi_{\rm fl})$ of OligoPV-TPA, OligoPV-C and OligoPV-T are measured in different solvents, by using Rhodamine B as a standard, presented in Table 1. We found the $\Phi_{\rm fl}$ values of OligoPV-TPA, OligoPV-C and OligoPV-T to be in the range of 0.18–0.23. It was found that the $\Phi_{\rm fl}$ value of OligoPV–C is higher than that of OligoPV-TPA and OligoPV-T in diluted solution. This may be due to the slight rotor nature of compound OligoPV-TPA and OligoPV-T *i.e.* triphenylamine/thiophene moiety undergoes active intramolecular rotations in the solution which effectively quenching the light emission. The HOMO-LUMO gaps (ΔE) of luminogens OligoPV-TPA, OligoPV-C and OligoPV-T are 3.48, 3.87 and 3.19 eV in toluene and 3.44, 3.82 and 3.19 eV in THF respectively. It is worth noting that the change of the substituent groups from triphenylamine, carbazole and thiophene moieties causes a little influence on band gap of compound. The emission spectra are also measured in the powdered state of the compounds (Fig. 1). Oligomer OligoPV-C exhibited red shifted (~30 nm) emission in the powdered state compared to those observed in THF or toluene solution (Table 1). Moreover, this derivative shows red shifted broad peak in the powdered state at around 534 nm indicates molecular aggregation or excimer formation in the solid state. The emission spectra of Oligomers OligoPV-TPA and OligoPV-T in powdered state displayed slightly red shifted peak about 7 nm and 17 nm respectively compare to solution state in toluene.

For determining the aggregation behavior of synthesized luminogens, the fluorescence behaviour of their diluted mixtures was studied in a mixture of water/THF under different water fractions.

Since the compounds were insoluble in water, increasing the water fraction in the mixed solvent could change their existing forms from a solution or well-dispersed state in THF to the aggregated particles in the aq. THF with high water content. Changes in the PL peak intensities *vs.* water fraction of the mixture for compound OligoPV–TPA were plotted, as shown in Fig. 1 as an example.

In THF-water mixtures with low water fraction ($f_w \le 40\%$), the fluorescence intensity remain unchanged. When f_w is higher than 40%, the solutions emit bright yellowish green light with λ_{em} at 519 nm upon photoexcitation. The pronounced fluorescence enhancement phenomenon can be interpreted as the aggregation of OligoPV-TPA molecules at higher f_w values. According to the above-mentioned RIR mechanism, when the OligoPV-TPA is dissolved in THF or THF-water mixtures with f_w \leq 40%, the active intramolecular rotations of multiple phenyl rings exhaust the energy of the excited states and result in fluorescence quenching. When more water, a nonsolvent for OligoPV-TPA, is added into the solution, the molecules tend to form aggregates, thus the intramolecular rotations of the phenyl rings are restricted and the excited states decay to the corresponding ground states through irradiative channels thereby strong emission is recorded. At the f_w of 70%, a

maximum fluorescence intensity has been recorded, and the corresponding amplification factor α_{AIEE} ($\alpha_{AIEE} = I_{aggr}/I_{soln}$) is 8.4. After reaching a maximum, PL intensities decreased with higher water content. This phenomenon was often observed in some compounds with AIEE properties, but the reason remains unclear.¹⁵ One possible explanation is that in a mixture with a "low" water fraction, solute molecules steadily assemble in an ordered pattern to form more emissive, crystalline aggregates. In a mixture with "high" water content, solute molecules quickly agglomerate in a random way to form less emissive, amorphous counterparts.¹⁶

Similar enhancement was observed for oligomer OligoPV–T. When the water fraction was increased from 0 to 90%, the fluorescence intensities of OligoPV–T were enhanced 5.8-fold (Fig. S2, ESI†). The measured PL intensity shows no regularity in high water content.¹⁷ The results indicate that the AIEE effect of the compound OligoPV–TPA is higher than that of OligoPV–T. But, compound OligoPV–C exhibited different phenomenon in aggregation study. In aggregate state, the emission behavior is quenched for OligoPV–C *i.e.*, when the water fraction was increased from 0 to 90%, the fluorescence intensity of OligoPV– C was correspondingly decreased (3.6-fold). This decrease in fluorescence intensity may be due the aggregation-caused quenching (ACQ) effect. Probably the planar architecture of OligoPV–C facilitates the ACQ in highly concentrated solution.

The thermal properties of the oligomers were analyzed by thermogravimetric analysis (TGA) and are presented in Table 1. These compounds exhibited good thermal stabilities. The decomposition temperatures with 5% weight loss under N₂ atmosphere (T_d) for OligoPV–TPA, OligoPV–C and OligoPV–T were 340, 390 and 352 °C, respectively (Fig. 1). The T_d values decreased with the increasing rotor nature of oligomers.

In summary, three new thermally stable OligoPV-cored luminogens were synthesized and characterized. Out of three, two are AIEE-active molecules: weakly fluorescent in solutions, while highly emissive in the aggregation state. The presence of the OligoPV core has endowed to turn an ACQ luminophore to an AIEE one. These properties suggest that *p*-phenylenevinylenecored luminogens can be employed in light-emitting application.

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