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# PAPER



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## Introduction

Highly luminescent  $\pi$ -conjugated organic molecules form the basis of optical and electronic devices such as organic lightemitting diodes (OLEDs),1 organic light-emitting field-effect transistors (OLEFETs)<sup>2</sup> and organic fluorescent sensors.<sup>3</sup> However, most  $\pi$ -conjugated molecules have very high efficiency in dilute solution but relatively weak emission in the solid state as intra- and intermolecular interactions quench the emission process.4 Several approaches such as dendritic or bulky substituent protection,<sup>5,6</sup> cross-dipole stacking,<sup>7</sup> aggregation-induced emission,<sup>8</sup> J-aggregate formation<sup>9</sup> and enhanced intramolecular charge-transfer transition<sup>10</sup> have been used to achieve an intense solid-state emission. A variety of organic molecules such as siloles,<sup>11,12</sup> 1-cyano-trans-1,2-bis-(4-methylbiphenyl)ethylene,<sup>13</sup> thienyl-azulene,<sup>14</sup> arylethene<sup>15</sup> and naphthalimide<sup>16</sup> derivatives that emit strongly in their aggregated or solid state have been reported. Various possible mechanisms including conformational planarization, J-aggregate formation, twisted intramolecular charge transfer (TICT) and restriction of intramolecular rotation (RIR) have been

# Pentacenequinone derivatives: aggregationinduced emission enhancement, mechanism and fluorescent aggregates for superamplified detection of nitroaromatic explosives<sup>†</sup>

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Pentacenequinone derivatives **5–9** have been synthesized by a Suzuki–Miyaura coupling protocol. These derivatives form fluorescent aggregates in mixed aqueous media due to their aggregation-induced emission enhancement (AIEE) attributes. Interestingly, size dependent emission enhancement is observed in the case of derivatives **5–7** and the effect of increase in the number of pyridine rotors on fluorescence emission of pentacenequinone derivatives **6–7** in solution and in the aggregate state confirms that the AIEE phenomenon is at the cost of aggregation driven growth and restriction of intramolecular rotation (RIR). On the other hand, derivatives **8** and **9** having electron rich phenyl groups are donor–accepter–donor type systems which exhibit an intermolecular charge transfer state (ICT) and form fluorescent aggregates in mixed aqueous media. In addition to this, the AIEE characteristics endow pentacenequinone derivatives **5–9** with sensing functionalities such as detection of nitroaromatic compounds. TLC strips of AIEE-active pentacenequinone derivatives **5–9** provide a more convenient and cost-effective approach for the trace detection of nitroaromatic explosives.

proposed for the increase in emission intensity in the aggregated state.<sup>17–21</sup> Thus, more investigation is needed to prove the actual mechanism for the aggregation-induced emission enhancement (AIEE) phenomenon.

Our research work involves design, synthesis and evaluation of organic materials having AIEE characteristics for the detection of various analytes.<sup>22-25</sup> In our previous reports, we have utilized the AIEE phenomena for the preparation of fluorescent aggregates. Further we utilized these aggregates for detection of nitroaromatic explosives viz. picric acid (PA) and trinitrotoluene (TNT). However, in none of these reports we have discussed the effect of nature and the number of rotors on the photophysical properties of these derivatives in the aggregated state. In addition, we have not discussed the reason of AIEE phenomena in these molecules. Since most of these reported derivatives form spherical aggregates, we could not study the relationship between morphology of these derivatives with their sensing sensitivity toward nitroaromatic explosives. In one of the published research work, we reported that pentacenequinone derivative 6 forms fluorescent aggregates in aqueous media due to its AIEE attributes.<sup>23</sup> We proposed that RIR<sup>26</sup> of the heteroaromatic ring at the periphery of the pentacenequinone core in the aggregated state is the main cause of the AIEE effect. To get more insight into the mechanism of AIEE, in the present manuscript, we have designed and synthesized a series of new AIEE-active molecules based on the pentacenequinone scaffold. We have chosen the pentacenequinone scaffold as it is rigid and

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is a planar molecule and has tendency to form ordered thin films which make it a good candidate for the preparation of organic electronic devices.27 We envisioned that varying the number of hetero-aromatic rotors on the pentacenequinone core would influence photophysical properties of the molecules which will be helpful in understanding the mechanism of AIEE and hence will provide the molecular designs for the preparation of fluorescent aggregates.<sup>28,29</sup> Thus, with this hypothesis in mind, we designed and synthesized mono, di and tetra substituted pentacenequinone derivatives 5-7. We observed that in the aggregated state emission intensity of these derivatives increased with increase in the number of pyridine rotors on the pentacenequinone core. Further, comparison of fluorescence studies of derivatives 6-7 suggests that the AIEE phenomenon is due to aggregation driven-growth and restriction of intramolecular rotation. In addition to this, we synthesized the pentacenequinone based derivatives 8 and 9 and found that these derivatives are donor-accepter-donor type systems which exhibit an intermolecular charge transfer state (ICT) and form fluorescent aggregates in mixed aqueous media. The presence of alkyl chains on pentacenequinone derivative 8 enhances the emission efficiency in the aggregated state as compared to derivative 9. Further, we utilized TLC strips coated with derivatives 5-9 for instant detection of nitroaromatic explosives.

#### Results and discussion

Pentacenequinone derivatives 5–7 were synthesized by Suzuki– Miyaura coupling of boronic ester  $4a^{30}$  with respective pentacenequinone derivatives 1–3 (ref. 31 and 32) (Scheme 1). The structures of derivatives 5, 6 (ref. 23) and 7 were confirmed from their spectroscopy and analytical data (Fig. S44–S47 in ESI†).

We evaluated the photophysical properties of pentacenequinone derivatives 5–7 by UV-vis and fluorescence spectroscopy. The UV-vis spectrum of derivative 5 in DMSO exhibits a characteristic absorption band at 310 nm corresponding to the  $\pi$ - $\pi$ \* transition of the pentacenequinone moiety (Fig. S1 in ESI†). On addition of water fractions (up to 50%) to the DMSO solution of derivative 5, a *level-off* long wavelength tail appears which is attributed to the Mie scattering due to the formation of aggregates<sup>33</sup> (Fig. S1 in ESI<sup> $\dagger$ </sup>). Similar results were obtained in the case of pentacenequinone derivatives **6** and **7** under the same set of conditions as used for derivative **5** (Fig. S2–S3 in ESI<sup> $\dagger$ </sup>).

In the fluorescence spectrum, the dilute solution of derivative 5 in DMSO exhibits a weak emission band ( $\Phi_{\rm F}^{34} = 0.030$ ) at 460 nm when excited at 310 nm (Fig. 1). However, a dramatic change in fluorescence emission intensity is observed in the H<sub>2</sub>O-DMSO mixture. On addition of 10% volume fraction of water an emission band appears at 468 nm. Addition of 30% volume fraction of water leads to enhancement of emission along with the red shift in the emission band from 468 nm to 481 nm ( $\Delta \lambda = 13$  nm). Further addition of water fractions up to 50% leads to enhancement in emission intensity which is clearly visible to the naked eye under the illumination of 365 nm (inset, Fig. 1). The scanning electron microscopy (SEM) analysis of derivative 5 in the H<sub>2</sub>O-DMSO (1 : 1, v/v) mixture showed the presence of irregular shaped aggregates (Fig. S4A in ESI<sup>+</sup>). The dynamic light scattering (DLS) studies clearly showed an average size around 660 nm, 440 nm and 220 nm in 10%, 30%, and 50% H<sub>2</sub>O-DMSO solvent mixtures of derivative 5 respectively (Fig. S4B in ESI<sup>†</sup>). We assume that as the particles tend to shrink in size with increasing water content in the solvent mixture,35 a more coplanar conformer imposed by the congested environment in the shrunk particles may be responsible for this bathochromic shift.

However, addition of more than 50% water fraction to DMSO solution of derivative 5 results in decrease in fluorescence emission intensity (Fig. S5 in ESI<sup>†</sup>). This phenomenon is often observed in derivatives with AIEE properties<sup>36</sup> as after the aggregation only the molecules on the surface of aggregates emit light and contribute to the fluorescent intensity upon excitation and this leads to a decrease in emission intensity.<sup>36</sup> We also carried out fluorescence studies of pentacenequinone derivatives **6** (ref. 23) and 7 under same set of conditions as used for derivative 5 (Fig. S5 and S6 in ESI<sup>†</sup>). Addition of water fractions up to 50% to the DMSO solution of derivative 7 leads to red shifting ( $\Delta \lambda = 28$  nm) of the emission band from 464 to 492 nm along with enhancement of the emission signal. The



Scheme 1 Pentacenequinone based derivatives 5–7.



Fig. 1 Fluorescence spectra of derivative 5 (10  $\mu$ M) showing the variation of fluorescence intensity in H<sub>2</sub>O-DMSO mixtures.  $\lambda_{ex} = 310$  nm. The inset photograph shows the fluorescence intensity at (a) 0% and (b) 50% water in DMSO.

DLS studies of derivative 7 in 10%, 30%, and 50% H<sub>2</sub>O–DMSO solvent mixtures showed aggregates of an average size around 305 nm, 550 nm and 768 nm, respectively (Fig. S7A in ESI<sup>†</sup>). The enhancement and red shifting of the emission signal are related to the aggregation driven growth of the aggregates<sup>14</sup> of derivative 7. A linear relationship between emission enhancement and size of aggregates of derivative 7 is observed (Fig. S8A in ESI<sup>†</sup>). Similar emission behaviour is observed in the case of derivative 6 (Fig. S7B and S8B in ESI<sup>†</sup>). The SEM image of derivative 6 showed irregular shaped aggregates whereas flake like morphology was observed in the case of derivative 7 (Fig. S9A and S9B in ESI<sup>†</sup>).

The quantum yield of aggregates of derivative 7 in  $H_2O$ -DMSO (1:1, v/v) increased to 0.43 which is 16 times higher than that in DMSO solution. In the case of derivative **6** and **5**, an increase of 14 and 7 times respectively is observed to that of their DMSO solutions.

To get insight into the mechanism of AIEE, we investigated the effect of variations in the viscosity and temperature on fluorescence behaviour of derivatives 5-7. For this, the fluorescence spectra of derivative 5 in the viscous mixture of DMSO and glycerol with different glycerol fractions were recorded (Fig. 2) and it was found that upon addition of 90% volume fraction of glycerol, the fluorescence intensity increases. This is attributed to high viscosity that hampers intramolecular rotation, leading to closure of the non-radiative decay channel, hence, making the molecule emissive. In a 50% DMSO-glycerol solvent mixture, increase in fluorescence emission is purely due to the viscosity effect as the derivative is soluble in this mixture. Abrupt increase in fluorescence intensity is observed in the presence of more than 50% volume fraction of glycerol in DMSO. This is due to the combined effect of viscosity and aggregation as molecules are less soluble in these mixtures. Similar results were obtained in the case of pentacenequinone derivatives 6 and 7 (Fig. S10 in ESI<sup>†</sup>).

To compare the increase in fluorescence intensity of these derivatives, we plotted the change in the peak intensity vs. glycerol content (Fig. S11 in ESI†). Interestingly, fluorescence intensity of derivative 7 increased by 11.8 times to that in pure DMSO solution (Table 1) compared to the 9.56 fold



Fig. 2 Fluorescence spectra of derivative 5 (5  $\mu$ M) showing the variation of fluorescence intensity in DMSO–glycerol mixtures with different glycerol fractions.

enhancement observed in the case of derivative **6**, 5.6 fold enhancement is observed in the case of **5**. This may be attributed to a greater degree of the restriction in rotation of a higher number of rotors.

We investigated the effect of temperature on the fluorescence spectra of derivative 5 in  $H_2O$ -DMSO (1 : 1, v/v) solvent mixture and found that fluorescence intensity decreases with increase in the temperature up to 75 °C which clearly shows conversion of the aggregated state to a monomer like state at high temperature (Fig. S12 in ESI<sup>†</sup>). At high temperature pyridine rotors of pentacenequinone derivatives 5-7 rotate fast which lead to a non-radiative decay process and hence make them less emissive. Similar results were obtained in the case of derivatives 6 and 7 (Fig. S13 in ESI<sup>†</sup>). The decrease in fluorescence intensity of derivative 7 with increase in solution temperature was up to 82%. On the other hand, decrease of 74% and 48% is observed in the case of derivatives 6 and 5 respectively (Table 1). The viscosity and temperature dependent studies suggest that RIR plays a crucial role in emission enhancement in the case of derivatives 5-7.

We carried out time resolved fluorescence studies to determine the life times of these derivatives in the aggregated state. The fluorescence life time data (Table 1) for derivatives 5-7 in the aggregated state were obtained by fitting the time resolved curves based on the double-exponential function. Although there is a small difference between fluorescence radiative rate constants<sup>37</sup> ( $K_{\rm f}$ ) of derivative 5 (0.733 × 10<sup>9</sup> s<sup>-1</sup>), 6 (0.251 × 10<sup>9</sup>  $s^{-1}$ ) and 7 (0.233  $\times$  10<sup>9</sup>  $s^{-1}$ ), the non-radiative decay constant  $(K_{\rm nr})$  of derivative 5 (2.6  $\times$  10<sup>9</sup> s<sup>-1</sup>) was larger than those of derivatives 6 (0.36  $\times$  10<sup>9</sup> s<sup>-1</sup>) and 7 (0.30  $\times$  10<sup>9</sup> s<sup>-1</sup>). These studies show that increase in the number of rotors accelerate the decrease in the non-emissive rate constant.<sup>37,38</sup> In the case of derivatives 6 and 7, in the aggregated state major fraction of molecules undergoes radiative decay through the slow pathway. On the other hand, in the case of derivative 5, 72% of molecules undergo radiative decay through the fast pathway. However, the decay time of derivative 5 in 50% water fraction (0.30 ns) is longer than that of 5 in 0% water fraction (0.081 ns) which implies formation of ordered aggregates.39 We also carried out the fluorescence anisotropy studies40-42 of derivative 7 which show an increase in the average anisotropy value of derivative 7 in DMSO from 0.05 to 0.32 in H<sub>2</sub>O-DMSO (1 : 1, v/v) (Fig. S14 and S15 in ESI<sup>†</sup>). This result suggests decreased molecular motion in the case of derivative 7 on aggregation.

In the next part of our investigation, we were interested in studying the effect of the presence of electron rich phenyl rotors instead of electron deficient rotors on the AIEE characteristics of pentacenequinone derivatives. In the view of this, we synthesized pentacenequinone derivatives **8** and **9** with or without an alkyl chain respectively by Suzuki–Miyaura coupling of boronic esters **4b**<sup>43</sup> and **4c**<sup>44</sup> with pentacenequinone derivatives were confirmed from their spectroscopy and analytical data (Fig. S48–S53 in ESI<sup>†</sup>).

We evaluated the aggregation behaviour of derivatives 8 and 9 by UV-vis and fluorescence spectroscopy. The absorption spectrum of dilute solution of derivative 8 in THF shows a

Table 1 Comparative photophysical properties of derivative 5-7

Derivative	$\lambda_{\max}^{a}$	Quantum yield $\left( arPsi_{ m F}  ight)^b$ in solution	Quantum yield $(\Phi_{\rm F})^c$ in aggregates	Emission enhancement	$I/I_0^{d}$	$(I - I_0)/$ $I_0  imes 100^e$	$A_1/A_2^{f}$	$\tau_{F1}^{g}(ns)$	$\tau_{F2}^{g}(ns)$	${K_{\rm f}}^h (10^9 { m s}^{-1})$	$\binom{K_{\rm nr}^{\ i}}{(10^9 \ {\rm s}^{-1})}$
5	481	0.030	0.22	$\begin{array}{l} 7.3 \left( {\Phi_{\rm F}}^c / {\Phi_{\rm F}}^b \right) \\ 14.13 \left( {\Phi_{\rm F}}^c / {\Phi_{\rm F}}^b \right) \\ 15.92 \left( {\Phi_{\rm F}}^c / {\Phi_{\rm F}}^b \right) \end{array}$	5.6	48	72/28	0.30	2.02	0.733	2.6
6	481	0.029	0.41		9.56	74	36/64	0.078	1.63	0.251	0.36
7	492	0.027	0.43		11.8	82	35/65	0.13	1.84	0.233	0.30

<sup>*a*</sup> Emission maximum (nm). <sup>*b*</sup> Solution in DMSO. <sup>*c*</sup> Aggregates in H<sub>2</sub>O–DMSO with 50 vol% of water. <sup>*d*</sup> Increase in fluorescence intensity in 90% volume fraction of glycerol in DMSO. <sup>*e*</sup> Decrease in % age fluorescence intensity with increase in temperature upto 75 °C in 50 vol% of water in DMSO. <sup>*f*</sup> A<sub>1</sub>, A<sub>2</sub>: fractional amount of molecules in each environment. <sup>*g*</sup>  $\tau_{F1}$  and  $\tau_{F2}$ : biexponential life time of aggregates in 50 vol% of water in DMSO. <sup>*h*</sup> Radiative rate constant ( $K_{f} = \Phi_{F}/\tau_{F}$ ).<sup>37</sup> Non-radiative rate constant ( $K_{nr} = (1 - \Phi_{F})/\tau_{F}$ ).<sup>37</sup>





characteristic absorption band at 300 nm corresponding to  $\pi$ - $\pi$ \* transition of the pentacenequinone moiety (Fig. S16A in ESI†). However, in the presence of water as co-solvent, a new absorption band at 420 nm is observed along with appearance of a level-off long wavelength tail (Fig. S16A in ESI†). This new band may be assigned to the intermolecular charge-transfer (ICT) state.<sup>4,45</sup> Similar results were obtained in the case of derivative **9** under the same set of conditions as used for derivative **8** (Fig. S16B in ESI†). We carried out SEM analysis of derivatives **8** and **9** which shows spherical aggregates in the H<sub>2</sub>O-THF mixture (Fig. S17A and S17B in ESI†).

Further, solution of derivative **8** in THF is weakly emissive when excited at 300 nm ( $\Phi_{\rm F} = 0.0039$ ). A dramatic change in fluorescence behaviour of derivative **8** is observed when water is added to the THF solution of derivative **8** (Fig. 3). The addition of the 60% volume fraction of water to the THF solution of derivative **8** shows dual emission along with enhancement of emission intensity (Fig. 3). The two emission maxima at 475 and 555 nm resulted from the locally excited state and the intermolecular charge-transfer state,<sup>45</sup> respectively. However, the abrupt increase in fluorescence intensity of the emission band at 555 nm is observed ( $\Phi_{\rm F} = 0.24$ ) on increasing the water content to 90%. This change is clearly visible to naked eye under the illumination of 365 nm light (inset, Fig. 3). We believe that formation of the ICT state and conformational fixation upon aggregate formation is the reason for emission enhancement.<sup>46</sup>

Similar results were obtained in the case of derivative **9** under the same set of conditions as used for derivative **8** (Fig. S18 in ESI<sup>†</sup>). We carried out the fluorescence life time studies of derivatives **8** and **9** to get insight into the nature of the excited state (Table S1 pS14 in ESI<sup>†</sup>). The time resolved

Fig. 3 Fluorescence spectra of  $8~(10~\mu\text{M})$  showing the variation of fluorescence intensity in H\_2O-THF mixtures with different water fractions. Inset photographs (under 365 nm UV-light) (a) in pure THF (b) with the addition of 90% water in THF.

fluorescence studies showed increase in life time of derivative 8 from 0.95 ns in THF solution to 3.53 ns in the aggregated state and a large increase in fluorescence rate constant from 4.07 imes $10^6$  s<sup>-1</sup> in solution to  $6.7 \times 10^7$  s<sup>-1</sup> in aggregated state (Table S2 pS14 in ESI<sup>†</sup>). Further, we monitored the fluorescence decay of derivative 8 in H2O-THF (7/3) at two different emission maxima<sup>45</sup> (Table S1 pS14 in ESI<sup>†</sup>). The  $\tau_{\rm F}$  values (2.82 and 3.07 ns) observed at 555 nm were correspondingly longer than those observed (0.28 and 1.96 ns) at 480 nm. Further, the decay times of 3.07 and 6.54 ns were measured when the H<sub>2</sub>O-THF ratios were 7/3 and 9/1, respectively. We believe that longer  $\tau_{\rm F}$  values originate from the ICT state as the charge transfer state of organic molecules generally exhibits a longer decay time as compared to the locally excited state. Interestingly, aggregates of derivative 9 showed higher life time (9.48 ns) than that of aggregates of derivative 8. This may be attributed to effective  $\pi$ -stacking of phenyl groups in the case of derivative 9 as the presence of alkyl side chains in derivative 8 prevents the interchain  $\pi$ -stacking.<sup>47</sup> These studies show that derivatives 8 and 9 are donor-acceptor-donor type systems exhibiting the ICT state and form fluorescent aggregates in mixed aqueous media.45,48 On the other hand, ICT phenomena is not observed in the case of derivatives 5-7 having electron deficient pyridine groups where aggregation driven-growth and RIR are the reasons of AIEE in these derivatives. Thus, the above results provide

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another approach to develop materials having high fluorescence efficiency in the aggregated state.

#### Detection of nitroaromatic explosives

Recently, detection of nitroaromatic explosives has become an important issue as they are considered to be environmental contaminants and toxic to the living organisms.<sup>49</sup> Thus, the detection of trace amounts of explosives is very important in combating terrorism, for maintaining the national security and providing environmental safety.50-53 The large scale use of explosives by terrorist groups has prompted the scientific community to develop novel sensing materials for their detection. Various methods are available for the detection of nitroaromatics, such as GC-MS, ion-mobility spectroscopy (IMS), surface enhanced Raman spectroscopy and various other spectroscopic techniques.54-59 However, these methods cannot be used in the field due to their high cost, lack of selectivity and sensitivity.<sup>60</sup> Fluorescence spectroscopy on the other hand is a highly sensitive technique hence one of the first choices for the detection of nitroaromatics.52 In recent years, chemical sensors with high sensitivity for the detection of derivatives such as trinitrotoluene (TNT), dinitrotoluene (DNT), RDX and picric acid (PA), have been reported.<sup>61</sup> However, most of the reported chemosensors work well in organic solvents.62-66 Thus, the development of sensitive chemosensors for the detection of nitro explosives which work well in the aqueous environment is still a challenge.

In view of this, we utilized the fluorescent aggregates of pentacenequinone derivatives 5–9 for the detection of nitroaromatic explosives in mixed aqueous media. For this, we carried out the fluorescence titrations of derivatives 5–7 in  $H_2O$ –DMSO (1 : 1) and 8/9 in  $H_2O$ –THF (9 : 1) mixtures toward various nitroderivatives such as PA, TNT, DNT, 1,4-dinitrobenzene (DNB), 1,4-dinitrobenzoic acid (DNBA), 1,4-benzoquinone (BQ), nitromethane (NM), and 2,3-dimethyl-2,3-dinitrobutane (DMDNB).

All the pentacenequinone derivatives **5–9** exhibit similar behaviour to that of nitroaromatic explosives and since pentacenequinone derivative 7 shows a higher quantum yield in its aggregate state and thus, we have focused our discussion on the nitroaromatic explosives sensing property of aggregates of derivative 7 in the following discussion. The addition of 58 equiv. of PA to the solution of 7 leads to significant quenching in fluorescence emission (Fig. 4) which is clearly visible to the naked eye under the illumination of UV light of 365 nm (inset, Fig. 4). Similar results were obtained with other pentacenequinone derivatives **5–9** upon addition of PA (Fig. S19–S23 in ESI†) and are summarized in Table 2.

Further, we studied the fluorescence emission response of aggregates of pentacenequinone derivatives **5–9** to PA by using a Stern–Volmer relationship. We observed a linear Stern–Volmer plot at a lower concentration of PA (Fig. S19–S23 in ESI<sup>†</sup>) which indicate that fluorescence quenching of aggregates of pentacenequinone derivatives **5–9** involves a static quenching through the excited state interaction.<sup>67</sup> However at a higher concentration of PA, the plot bents upwards (Fig. S19–S23 in ESI<sup>†</sup>), thus,



Fig. 4 Change in fluorescence spectra of compound 7 (10  $\mu$ M) with the addition of PA in the H<sub>2</sub>O–DMSO (1 : 1) mixture; the inset showing the fluorescence change (a) before and (b) after the addition of PA.

indicating a superamplified quenching effect.<sup>68,69</sup> These results suggest that the observed fluorescence quenching of the fluorescent aggregates is attributed to the electron transfer and/or energy transfer quenching mechanism.<sup>53,70</sup> We measured fluorescence life time of aggregates of derivatives **5–9** in the absence and presence of PA (Fig. S24–S28 in ESI†). The fluorescence lifetimes of aggregates of **5–9** were found to be invariant at different concentrations of PA thus, indicating that the aggregates of **5–9** decay mainly through the static pathway.<sup>71,72</sup>

Further, the spectral overlap between the absorption spectrum of PA and the emission spectrum of aggregates in the wavelength region of 420-480 nm (Fig. S29-S33 in ESI<sup>+</sup>) allows the energy transfer from the excited state of aggregates of derivatives 5-9 to the ground state to PA, further increasing the fluorescence quenching efficiency.53,73,74 The Stern-Volmer constant of derivative 7 at a lower concentration of PA is found to be  $6.52 \times 10^3$  M<sup>-1</sup>. The detection limit of derivative 7 for PA is calculated to be 600 nM. The better detection level in the case of derivative 7 as compared to derivatives 5 and 6 is due to the presence of a flake like structure in derivative 7 which is formed by entangled piling of the aggregates (Fig. S9B in ESI<sup>†</sup>).<sup>75</sup> The flake like structure provides the increase in porosity as well as a large surface area which leads to good contact with the explosives and enhances the sensing sensitivity.75,76 However, in the case of derivatives 5 and 6 irregular aggregates are observed (Fig. S4A and S9A in ESI<sup>†</sup>) which prefer to accumulate in a compact manner which leads to less porosity, hence, lower sensitivity was observed.75 The Stern-Volmer constants and detection limits for PA with other pentacenequinone derivatives are summarized in Table 2 and a lower detection limit in the

Derivative	PA (equiv.)	Stern–Volmer constant (in M <sup>–1</sup> )	Detection limit (in nM)
5 <sup><i>a</i></sup>	62	$3.40 imes10^3$	720
<b>6</b> <sup><i>a</i></sup>	60	$4.36 imes10^3$	650
<b>7</b> <sup><i>a</i></sup>	58	$6.52 imes10^3$	600
$8^{b}$	40	$8.44\times10^3$	250
<b>9</b> <sup>b</sup>	40	$3.61  imes 10^3$	290

<sup>*a*</sup> In H<sub>2</sub>O–DMSO (1 : 1). <sup>*b*</sup> In H<sub>2</sub>O–THF (9 : 1).



**Fig. 5** Photographs of compound **7** on test strips (a) before and (b) after dipping into aqueous solutions of PA.



Fig. 6 Photographs (under 365 nm UV light) of fluorescence quenching of aggregates of derivative 7 on test strips for the visual detection of a small amount of PA (A) test strip; PA of different concentrations: (b)  $10^{-4}$  M, (c)  $10^{-6}$  M, (d)  $10^{-8}$  M.

case of derivative **8** indicates that the presence of alkyl chains provides big cavities which allow PA molecules to diffuse more quickly.<sup>47,77</sup> Thus, derivative **8** shows good sensitivity to PA. The quenching in fluorescence emission of derivatives **5–9** was also observed with TNT, DNT, DNB, DNBA, BQ, NM, and DMDNB. The results of fluorescence studies of derivatives **5–9** with PA, TNT, DNT, DNB, DNBA, BQ, NM, and DMDNB are summarized in Fig. S34 and S35 in the ESI.<sup>†</sup> From these data we may conclude that fluorescent aggregates of derivatives **5–9** are sensitive for the detection of nitroaromatic explosives.

Further, for practical applications we have utilized the fluorescent aggregates for the detection of nitroaromatic explosives in the solid state. For this we prepared test strips by dip-coating solution of pentacenequinone derivatives **5–9** on TLC strips followed by drying the strips under vacuum. TLC strips of AIEEactive pentacenequinone derivatives show strong emission which becomes non-emissive when dipped into aqueous solution of PA which can be observed by naked eye (Fig. 5 and S36– S39 in ESI†). For detection of very small amounts of PA, we prepared the aqueous solutions of PA of different concentrations and 3  $\mu$ L of each solution were placed on **5–9** test strips (Fig. 6 and S40–S43 in ESI†).

Dark spots of different strengths were formed, which shows the practical applicability of test strips by varying the concentration of PA even up to a  $10^{-8}$  M level. Thus, these results show that derivatives **5–9** are excellent chemosensors for the instant visualization of the trace amount of PA in solution as well as in the solid state.

#### Conclusions

In conclusion, we synthesized pentacenequinone derivatives **5–9** by a Suzuki–Miyaura coupling strategy. Emission intensity of derivatives **5–7** increased in the aggregated state with increase in the number of pyridine rotors on the pentacenequinone core. Further, fluorescence studies of derivatives **6–7** suggest that aggregation driven-growth along with restriction of intramolecular rotation are the main causes of the AIEE phenomenon. On the other hand, derivatives **8–9** having phenyl groups are donor–accepter–donor type systems which exhibit an intermolecular charge transfer state and form fluorescent aggregates due to conformational fixation upon aggregate formation in mixed aqueous media. In addition to this, aggregates of derivatives **5–9** can detect nitroaromatic explosives in mixed aqueous media. Pentacenequinone derivative **8** having an alkyl chain showed a better detection limit as compared to derivative **9**, thus, providing another molecular design for increasing the sensitivity of the molecule. We also utilized TLC strips coated with derivatives **5–9** for instant detection of nitroaromatic explosives which provide a simple, portable and low cost method for the detection of nitroaromatic explosives.

### **Experimental section**

General experimental procedure: please see pS3 in ESI.†

General procedure for the synthesis of derivatives 5, 7–9: (compound 6 was synthesised by reported method<sup>23</sup>)

To a solution of 1/3/2/2 (0.5/0.5/0.5/0.5 g, 1.3/0.80/1.07/2.45 mmol) and 4a/4a/4b/4c (0.293/0.699/0.72/0.457 g, 1.43/3.36/2.25/0.98 mmol) in 20 mL of 1,4-dioxane were added K<sub>2</sub>CO<sub>3</sub> (0.359/0.885/1.18/1.08 g, 2.6/6.41/8.56/7.84 mmol), distilled H<sub>2</sub>O (1.3/3.2/3/3 mL) and Pd(Cl)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(0.2/0.123/0.273/0.249 g, 0.286/0.176/0.236/0.215 mmol) under N<sub>2</sub>, and the reaction mixture was then refluxed overnight. After completion of the reaction (TLC), the mixture was cooled to room temperature. 1,4-Dioxane was then removed under vacuum, and the residue so obtained was treated with water, extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was evaporated and the compound was purified by column chromatography to give compound 5/7/8/9.

Derivative 5: chloroform–methanol (97 : 3); 60%yield; M.Pt. >260 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.46–7.50 (m, 1H, ArH), 7.70–7.73 (m, 2H, ArH), 7.91–7.95 (m, 1H, ArH), 8.03–8.07 (m, 1H, ArH), 8.11–8.15 (m, 2H, ArH), 8.22–8.30 (m, 2H, ArH), 8.69 (d, 1H, *J* = 3.3 Hz, ArH), 8.95 (s, 2H, ArH), 8.97 (s, 1H, ArH), 9.01 (s, 1H, ArH), 9.02 (s, 1H, ArH); TOF MS ES+: 386.2; due to poor solubility of compound 5, its <sup>13</sup>C NMR spectrum could not be recorded. Elemental analysis: calcd for C<sub>27</sub>H<sub>15</sub>NO<sub>2</sub>: C, 84.14%; H, 3.92%; N, 3.63%; found: C, 84.05%; H, 3.62%; N, 3.60%.

Derivative 7: chloroform–methanol (97 : 3); 30% yield; M.Pt. >260 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.28 (s, 4H, ArH), 7.49–7.52 (m, 4H, ArH), 8.24 (s, 4H, ArH), 8.59 (s, 8H, ArH), 9.06 (s, 4H, ArH); TOF MS ES+: 617.3 (M + 1)<sup>+</sup>; due to poor solubility of compound 7, its <sup>13</sup>C NMR spectrum could not be recorded. Elemental analysis: calcd for C<sub>42</sub>H<sub>24</sub>N<sub>4</sub>O<sub>2</sub>: C, 81.80%; H, 3.92%; N, 9.09%; found: C, 81.75%; H, 3.62%; N, 9.00%.

[m, 2H, ArH], 8.09 [s, 2H, ArH], 8.11–8.15 (m, 2H, ArH), 8.94 [s, 2H, ArH], 8.95 (s, 2H, ArH); <sup>13</sup>C-NMR  $\delta$  (75.45 MHz, CDCl<sub>3</sub>): 14.04, 22.62, 25.76, 29.27, 31.62, 68.04, 100.14, 114.49, 129.47, 129.78, 130.08, 130.60, 130.69, 130.95, 131.14, 132.63, 134.40, 135.30, 142.75, 158.53, 182.99; TOF MS ES+: 685.4335 (M + Na + 2)<sup>+</sup>; elemental analysis: calcd for C<sub>46</sub>H<sub>44</sub>O<sub>4</sub>: C, 83.60%; H, 6.71%; found: C, 83.55%; H, 6.60%.

Derivative **9**: chloroform–hexane (1 : 1); 40% yield; M.Pt. >260 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.29 [s, 2H, ArH], 7.69–7.72 [m, 6H, ArH], 8.11–8.15 [m, 6H, ArH], 8.94 [s, 4H, ArH], 8.97 (s, 2H, ArH). <sup>13</sup>C-NMR  $\delta$  (75.45 MHz, CDCl<sub>3</sub>): 127.32, 128.13, 129.49, 129.61, 129.81, 129.86, 130.14, 130.41, 130.63, 130.93, 131.46, 135.30, 140.33, 142.97, 183.01. TOF MS ES+: 482.2296 (M + Na)<sup>+</sup>; elemental analysis: calcd for C<sub>32</sub>H<sub>20</sub>O<sub>2</sub>: C, 88.67%; H, 4.38%; found: C, 88.68%; H, 4.36%.

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### Notes and references

- R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund and W. R. Salaneck, *Nature*, 1999, **397**, 121–128.
- 2 J. Zaumseil and H. Sirringhaus, *Chem. Rev.*, 2007, **107**, 1296–1323.
- 3 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402–428.
- 4 B. K. An, S. K. Kwon, S. D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, **124**, 14410–14415.
- 5 J. Wang, Y. Zhao, C. Dou, H. Sun, P. Xu, K. Ye, J. Zhang, S. Jiang, F. Li and Y. Wang, *J. Phys. Chem. B*, 2007, **111**, 5082–5089.
- 6 H. Langhals, O. Krotz, K. Polborn and P. Mayer, Angew. Chem., Int. Ed., 2005, 44, 2427–2428.
- 7 Z. Xie, B. Yang, F. li, G. Cheng, L. Liu, G. Yang, H. Xu, L. Ye,
   M. Hanif, S. Liu, D. Ma and Y. Ma, *J. Am. Chem. Soc.*, 2005,
   127, 14152–14153.
- 8 Y. Dong, J. W. Y. Lam, A. Qin, J. Sun, J. Liu, Z. Li, J. Sun, H. H. Y. Sung, I. D. Williams, H. S. Kwok and B. Z. Tang, *Chem. Commun.*, 2007, 3255–3257.
- 9 T. E. Kaiser, H. Wang, V. Stepanenko and F. Wurthner, Angew. Chem., Int. Ed., 2007, **119**, 5637–5640.
- 10 M. Shimizu, Y. Takeda, M. Higashi and T. Hiyama, *Angew. Chem., Int. Ed.*, 2009, **48**, 3653–3656.
- 11 G. Yu, S. 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**, 6335–6346.
- 12 J. Chen, H. Peng, C. C. W. Law, Y. Dong, J. W. Y. Lam, I. D. Williams and B. Z. Tang, *Macromolecules*, 2003, 36, 4319–4327.

- 13 B. K. An, D. S. Lee, Y. S. Park, H. S. Song and S. Y. Park, *J. Am. Chem. Soc.*, 2004, **126**, 10232–10233.
- 14 F. Wang, M. Y. Han, K. Y. Mya, Y. Wang and Y. H. Lai, *J. Am. Chem. Soc.*, 2005, **127**, 10350–10355.
- 15 K. Itami, Y. Ohashi and J. I. Yoshida, *J. Org. Chem.*, 2005, **70**, 2778–2792.
- 16 H. H. Lin, Y. C. Chan, J. W. Chen and C. C. Chang, J. Mater. Chem., 2011, 21, 3170–3177.
- 17 L. Yang, J. Ye, X. Xu, L. Yang, W. Gong, Y. Lin and G. Ning, *RSC Adv.*, 2012, **2**, 11529–11535.
- 18 X. Du and Z. Y. Wang, Chem. Commun., 2011, 47, 4276-4278.
- 19 X. Zhang, Z. Chi, B. Xu, L. Jiang, X. Zhou, Y. Zhang, S. Liu and J. Xu, *Chem. Commun.*, 2012, **48**, 10895–10897.
- 20 S. J. Yoon, J. W. Chung, J. Gierschner, K. S. Kim, M. G. Choi, D. Kim and S. Y. Park, *J. Am. Chem. Soc.*, 2010, **132**, 13675– 13683.
- 21 X. Q. Zhang, Z. G. Chi, B. J. Xu, C. J. Chen, X. Zhou, Y. Zhang, S. W. Liu and J. R. Xu, *J. Mater. Chem.*, 2012, 22, 18505– 18513.
- 22 V. Bhalla, A. Gupta and M. Kumar, *Org. Lett.*, 2012, **12**, 3112–3115.
- 23 V. Bhalla, A. Gupta and M. Kumar, *Chem. Commun.*, 2012, **48**, 11862–11864.
- 24 M. Kumar, V. Vij and V. Bhalla, *Langmuir*, 2012, **28**, 12417–12421.
- 25 V. Bhalla, S. Pramanik and M. Kumar, *Chem. Commun.*, 2013, 49, 895–897.
- 26 Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332–4353.
- 27 I. Salzmann, D. Nabok, M. Oehzelt, S. Duhm, A. Moser,
  G. Heimel, P. Puschnig, C. A. Draxl, J. P. Rabe and
  N. Koch, *Cryst. Growth Des.*, 2011, 11, 600–606.
- 28 Q. Zhao, X. A. Zhang, Q. Wei, J. Wang, X. Y. Shen, A. Qin, J. Z. Sun and B. Z. Tang, *Chem. Commun.*, 2012, 48, 11671– 11673.
- 29 Q. Zeng, Z. Li, Y. Dong, C. Di, A. Qin, Y. Hong, L. Ji, Z. Zhu, C. K. W. Jim, G. Yu, Q. Li, Z. Li, Y. Liu, J. Qin and B. Z. Tang, *Chem. Commun.*, 2007, 70–72.
- 30 W. Li, D. P. Nelson, M. S. Jensen, R. S. Hoerrner, D. Cai, R. D. Larsen and P. J. Larsen, *J. Org. Chem.*, 2002, 67, 5394–5397.
- 31 C. R. Swartz, S. R. Parkin, J. E. Bullock, J. E. Anthony, A. C. Mayer and G. G. Malliaras, *Org. Lett.*, 2005, 7, 3163– 3166.
- 32 K. N. Plunkett, K. Godula, C. Nuckolls, N. Tremblay, A. C. Whalley and S. Xiao, *Org. Lett.*, 2009, **11**, 2225–2228.
- 33 B. Z. Tang, Y. Geng, J. W. Y. Lam, B. Li, X. Jing, X. Wang,
  F. Wang, A. B. Pakhomov and X. X. Zhang, *Chem. Mater.*,
  1999, 11, 1581–1589.
- 34 J. N. Demas and G. A. Grosby, *J. Phys. Chem.*, 1971, 75, 991–1024.
- 35 S. Jang, S. G. Kim, D. Jung, H. Kwon, J. Song, S. Cho, Y. C. Ko and H. Sohn, *Bull. Korean Chem. Soc.*, 2006, **27**, 12.
- 36 S. Dong, Z. Li and J. Qin, J. Phys. Chem. B, 2009, 113, 434-441.
- 37 Y. Kubota, S. Tanaka, K. Funabiki and M. Matsui, *Org. Lett.*, 2012, 14, 4682–4685.

- 38 Y. Ren, J. W. Y. Lam, Y. Dong, B. Z. Tang and K. S. Wong, J. Phys. Chem. B, 2005, 109, 1135–1140.
- 39 H. Tong, Y. Hong, Y. Dong, Y. Ren, M. Haussler, J. W. Y. Lam, K. S. Wong and B. Z. Tang, *J. Phys. Chem. B*, 2007, **111**, 2000– 2007.
- 40 Y.-B. Ruan, A. Depauw and I. Leray, *Org. Biomol. Chem.*, 2014, 12, 4335–4341.
- 41 C. E. Crespo-Hernandez, B. Cohen, P. M. Hare and B. Kohler, *Chem. Rev.*, 2004, **104**, 1977–2019.
- 42 H. Lee, C. W. Cone, B. Vanden and A. David, *J. High School Res.*, 2010, 1, 12–19.
- 43 X. Wang, J. Yan, Y. Zhou and J. Pei, *J. Am. Chem. Soc.*, 2010, 132, 15872–15874.
- 44 M. Murata, T. Oyama, S. Watanabe and Y. Masuda, *J. Org. Chem.*, 2000, **65**, 164–168.
- 45 R. M. Adhikari, B. K. Shah, S. S. Palayangoda and D. C. Neckers, *Langmuir*, 2009, **25**, 2402–2406.
- 46 Y. Shigemitsu, T. Mutai, H. Houjou and K. Araki, *J. Phys. Chem. A*, 2012, **116**, 2041–12048.
- 47 H. Nie, G. Sun, M. Zhang, M. Baumgarten and K. Mullen, J. Mater. Chem., 2012, 22, 2129–2132.
- 48 S. Choi, J. Bouffardb and Y. Kim, *Chem. Sci.*, 2014, 5, 751–755.
- 49 M. M. Qasim, B. Moore, L. Taylor, P. Honea, L. Gorb and J. Leszczynski, *Int. J. Mol. Sci.*, 2007, **8**, 1234–1264.
- 50 Z. Z. Rose, C. F. Madigan, T. M. Swager and V. Bulovic, *Nature*, 2005, **434**, 876–879.
- 51 H. Sohn, M. J. Sailor, D. Magde and W. C. Trogler, J. Am. Chem. Soc., 2003, **125**, 3821–3830.
- 52 D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537–2574.
- 53 S. W. Thomas III, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339–1386.
- 54 D. S. Moore, Rev. Sci. Instrum., 2004, 75, 2499-2513.
- 55 A. W. Czarnik, Nature, 1998, 394, 417-418.
- 56 K. R. Hakansson, V. Coorey, R. A. Zubarev, V. L. Talrose and P. Hakansson, *J. Mass Spectrom.*, 2000, **35**, 337–346.
- 57 J. M. Sylvia, J. A. Janni, J. D. Klein and K. M. Spencer, *Anal. Chem.*, 2000, 72, 5834–5840.
- 58 V. P. Anferov, G. V. Mozjoukhine and R. Fisher, *Rev. Sci. Instrum.*, 2000, **71**, 1656.

- 59 R. D. Luggar, M. J. Farquharson, J. A. Horrocks and R. J. Lacey, *X-Ray Spectrom.*, 1998, 27, 87–94.
- 60 E. Wallis, T. M. Griffin, N. Popkie, M. A. Eagan, R. F. Mcatee, D. Vrazel and J. McKinly, *Proc. SPIE*, 2005, 54, 5795.
- 61 M. E. Germain and M. J. Knapp, *Chem. Soc. Rev.*, 2009, **38**, 2543–2555.
- 62 A. Rana and P. K. Panda, RSC Adv., 2012, 2, 12164-12168.
- 63 N. Venkatramaiah, S. Kumar and S. Patil, *Chem.-Eur. J.*, 2012, **18**, 14745–14751.
- 64 S. Shanmugaraju, D. Samanta, B. Gole and P. S. Mukherjee, *Dalton Trans.*, 2011, **40**, 12333–12341.
- 65 Y. H. Lee, H. Liu, J. Y. Lee, S. H. Kim, S. K. Kim, J. L. Sessler,
  Y. Kim and J. S. Kim, *Chem.-Eur. J.*, 2010, 16, 5895–5901.
- 66 N. Venkatramaiah, S. Kumar and S. Patil, *Chem. Commun.*, 2012, **48**, 5007–5009.
- 67 D. Zhao and T. M. Swager, *Macromolecules*, 2005, 38, 9377– 9384.
- 68 J. Wang, J. Mei, W. Yuan, P. Lu, A. Qin, J. Sun, Y. Ma and B. Z. Tang, *J. Mater. Chem.*, 2011, 21, 4056–4059.
- 69 D. Li, J. Liu, R. T. K. Kwok, Z. Liang, B. Z. Tang and J. Yu, *Chem. Commun.*, 2012, **48**, 7167–7169.
- 70 Z. F. An, C. Zheng, R. F. Chen, J. Yin, J. J. Xiao, H. F. Shi, Y. Tao, Y. Qian and W. Huang, *Chem.-Eur. J.*, 2012, 18, 15655–15661.
- 71 H. Sohn, M. J. Sailor, D. Magde and W. C. Trogler, J. Am. Chem. Soc., 2003, 125, 3821–3830.
- 72 Y. Long, H. Chen, Y. Yang, H. Wang, Y. Yang, N. Li, K. Li, J. Pei and F. Liu, *Macromolecules*, 2009, **42**, 6501–6509.
- 73 W. Wu, S. Ye, L. Huang, L. Xiao, Y. Fu, Q. Huang, G. Yu, Y. Liu, J. Qin, Q. Lia and Z. Li, *J. Mater. Chem.*, 2012, 22, 6374–6382.
- 74 A. Qin, J. W. Y. Lam, L. Tang, C. K. W. Jim, H. Zhao, J. Sun and B. Z. Tang, *Macromolecules*, 2009, 42, 1421–1424.
- 75 X. Liu, X. Zhang, R. Lu, P. Xue, D. Xu and H. Zhou, *J. Mater. Chem.*, 2011, **21**, 8756–8765.
- 76 Z. Ding, Q. Zhao, R. Xing, X. Wang, J. Ding, L. Wang and Y. Han, J. Mater. Chem. C, 2013, 1, 786–792.
- 77 H. Li, J. X. Wang, Z. L. Pan, L. Y. Cui, L. Xu, R. M. Wang,
  Y. L. Song and L. Jiang, *J. Mater. Chem.*, 2011, 21, 1730– 1735.