

Fluorescent Nanoaggregates of Pentacenequinone Derivative for Selective Sensing of Picric acid in Aqueous Media

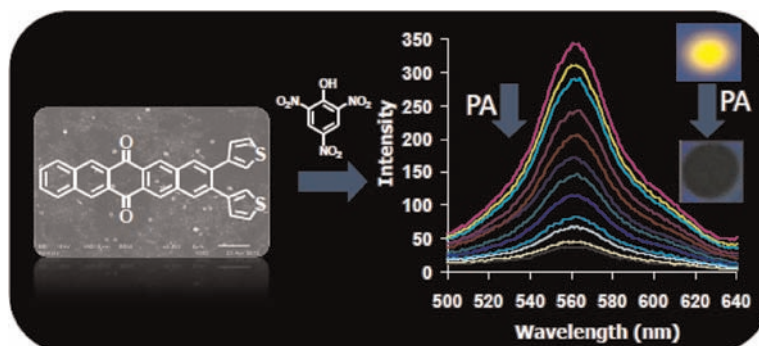
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ABSTRACT



Novel pentacenequinone derivative **3** has been synthesized using the Suzuki–Miyaura coupling protocol which forms fluorescent nanoaggregates in aqueous media due to its aggregation-induced emission enhancement attributes and selectively senses picric acid with a detection limit of 500 ppb.

Recently, fluorescent organic nanoparticles (FONs) have attracted considerable research interest, and those from perylene, pyrazoline, and carbazole have been reported.^{1,2} FONs hold higher potential as nanosized organic light-emitting diodes (OLEDs) and organic fluorescent sensors.^{3,4} Keeping in mind the potential of these FONs, we were interested in preparation of fluorescent organic molecules which spontaneously assemble into FONs. Pentacenequinone is a molecule of interest as pentacenequinone derivatives are important precursors for the synthesis of solution-processable pentacene derivatives which are promising candidates for organic electronic devices. In this context, preparation of highly fluorescent nanoparticles

of pentacenequinone derivatives could be beneficial. Pentacenequinone (acceptor) itself is weakly fluorescent; we envisioned that the thiophene groups (donor) at the periphery of a rigid π -conjugated framework could give a donor–acceptor–donor triad which may induce an intramolecular charge-transfer transition, efficiently suppressing self-quenching, and thus could provide another novel molecular design for emissive organic nanoparticles. Interestingly, the pentacenequinone derivative **3** exhibits aggregation-induced emission enhancement (AIEE) characteristics. Previously, a variety of organic molecules such as

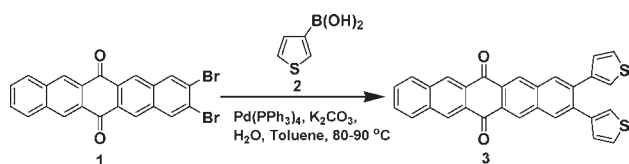
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siloles,⁵ thienylazulene,⁶ arylolethene,⁷ and naphthalimide⁸ derivatives that emit strongly in their aggregate or solid state have been reported. In addition, nanoaggregates of derivative **3** act as selective fluorogenic sensor for picric acid (PA) in aqueous media.

Suzuki–Miyaura coupling of 2,3-dibromopentacenequinone **1**⁹ with boronic acid **2** furnished pentacenequinone derivative **3** in 55% yield (Scheme 1). The ¹H NMR spectrum of compound **3** showed two singlets (2H, 4H) at 8.18 and 8.96 ppm, one doublet (2H) at 6.90 ppm, three multiplets (4H, 2H, 2H) at 7.24–7.29, 7.70–7.74 and 8.13–8.16 ppm corresponding to aromatic protons (see Figure S13, Supporting Information). The mass spectrum of compound **3** showed a parent ion peak at *m/z* 473.2 (*M* + 1)⁺ (see Figure S15, Supporting Information). These spectroscopic data corroborate the structure **3** for this compound.

Scheme 1. Pentacenequinone-Based Compound **3** Derived from **1**



The UV–vis spectrum of compound **3** in THF exhibits absorption bands at 415, 328, and 300 nm (Figure 1). On addition of water ($\leq 50\%$ volume fractions) to the THF solution of derivative **3**, the intensity of absorption bands is increased. However, a further increase of water content up to 90% leads to appearance of level-off long wavelength tail, which is attributed to the Mie scattering due to formation of nanoaggregates.¹⁰ The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of compound **3** in the solvent mixture of H₂O/THF with 90% volume fractions of water show the presence of spherical nanoaggregates (Figure 2 and see Figure S1, Supporting Information).

Confocal microscopy image also indicates the presence of fluorescent nanoparticles in solvent mixture of H₂O/THF (9:1) (Figure 2C). The nanoaggregates formed are visibly transparent and stable at room temperature for several months. Thus, TEM, SEM, and confocal studies support our UV–vis study for the formation of nanoaggregates.

In the fluorescence spectrum, compound **3** exhibits weak emission at 460 nm ($\Phi_F = 0.2$)¹¹ when excited at 328 nm (Figure 3A). A dramatic change in fluorescence behavior

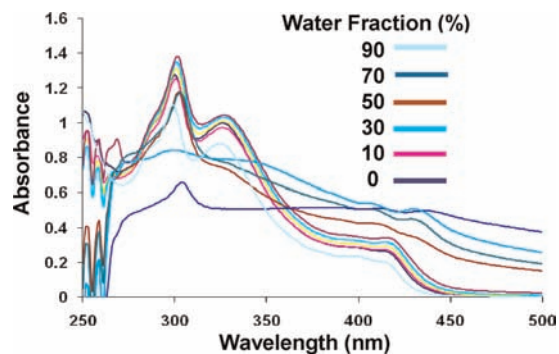


Figure 1. Absorption spectra of compound **3** (10 μ M) showing the variation of absorption intensity in a H₂O/THF mixture with different water fractions.

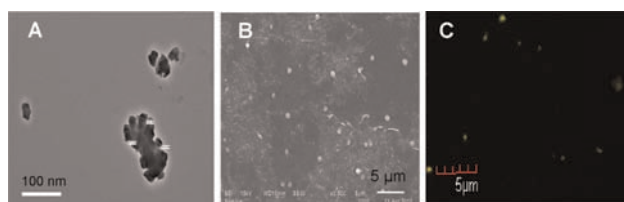


Figure 2. (A) TEM and (B) SEM images of **3** nanoaggregates obtained from a suspension that contained 90% volume fraction of water in THF. (C) Confocal microscope image of nanoaggregates of compound **3** in H₂O/THF (9:1 v/v) mixtures. $\lambda_{ex} = 405$ nm.

of compound **3** is observed when water is added to the THF solution of compound **3**. On addition of 10% volume fraction of water, enhancement of emission intensity is observed along with a red shift in the emission band to 492 nm. Further addition of the water fraction up to 50% leads to decrease in emission intensity accompanied by broadening of the emission band (Figure 3A). Upon addition of 60% volume fraction of water, the emission intensity increases swiftly and the emission band is red-shifted to 560 nm (at 60% H₂O/THF mixture), and nearly a 2-fold enhancement ($\Phi_F = 0.4$) in emission intensity is observed on increasing the water content to 90% (Figure 3B). The appearance of a red-shifted, sharp emission band with large shift (100 nm) suggests the formation of aggregates of the derivative **3** in H₂O/THF (9:1) mixture (Figure 3B). This is in agreement with observation of level-off long wavelength tail in the absorption spectrum (vide supra) (Figure 1). Derivative **3** is donor–acceptor–donor type

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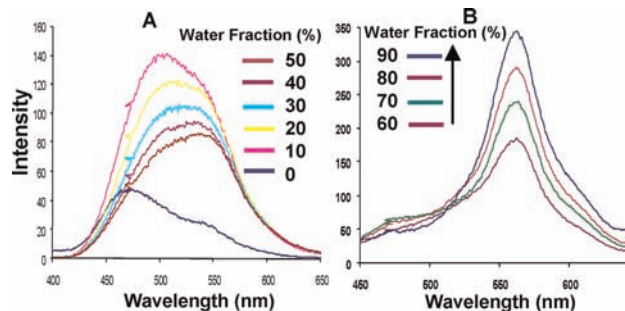


Figure 3. Fluorescence spectra of compound **3** ($10\ \mu\text{M}$) showing the variation of fluorescence intensity in $\text{H}_2\text{O}/\text{THF}$ mixture: (A) from 0 to 50%; (B) from 60 to 90% volume fractions of water in THF. $\lambda_{\text{ex}} = 328\ \text{nm}$.

system, and such types of systems tend to adopt a twisted conformation in more polar solvents and exhibit a twisted intramolecular charge-transfer state in the excited state which is susceptible to various nonradiative quenching processes;¹² hence, a decrease in emission intensity is observed by diluting with up to 50% volume fraction of water before the formation of aggregates. However, upon further addition of 60% of water fraction or higher the molecules of derivative **3** forms aggregates, which results in restriction of the intramolecular rotation. This restriction of intramolecular rotation, rigidifies the molecule and hence, makes it more emissive. The concentration dependent emission spectrum of compound **3** in THF also corroborates enhancement in emission on aggregation (see Figure S2, Supporting Information).

The strong emission of nanoaggregates of pentacene-quinone derivative **3** prompted us to explore their potential application as chemosensors for the detection of nitroaromatics such as trinitrotoluene (TNT), trinitrobenzene (TNB), picric acid (PA), etc., which are well-known primary constituents of many unexploded land mines worldwide. The detection of nitroaromatics has attracted a lot of attention as an effort to better combat terrorism and environmental safety.¹³ Further, among various techniques used for detection of nitroaromatics, fluorescence-based detection offers several advantages with respect to

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high sensitivity, specificity, and real-time monitoring with short response time.¹⁴

Thus, we carried out the fluorescence titrations of compound **3** ($10\ \mu\text{M}$) in an $\text{H}_2\text{O}/\text{THF}$ (9:1) mixture toward various nitroderivatives such as picric acid (PA), 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), 1,4-dinitrobenzene (DNB), 1,4-dinitrobenzoic acid (DNBA), 1,4-benzoquinone (BQ), nitromethane (NM), and 2,3-dimethyl-2,3-dinitrobutane (DMDNB). Upon addition of incremental amounts of $3\ \mu\text{M}$ of picric acid to the solution of **3** in $\text{H}_2\text{O}/\text{THF}$ (9:1) mixture, the quenching in fluorescence emission is observed at concentration as low as 35 equivalents (Figure 4A). The emission response to PA was studied by using Stern–Volmer relationship and linear plot (inset Figure 4B) with a Stern–Volmer constant of $6.9 \times 10^4\ \text{M}^{-1}$ was found when the concentration of PA was below $150\ \mu\text{M}$.

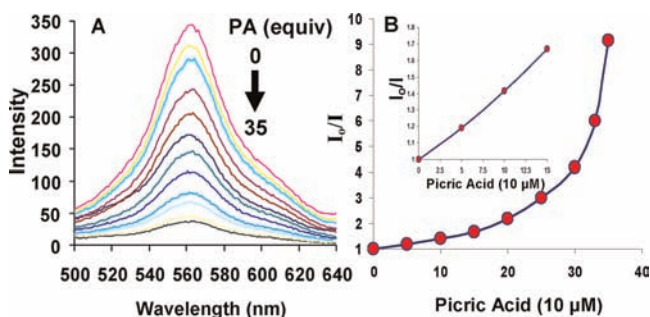


Figure 4. (A) Change in fluorescence spectra of compound **3** ($10\ \mu\text{M}$) with the addition of PA in $\text{H}_2\text{O}/\text{THF}$ (9:1) mixture; (B) Stern–Volmer plot in response to PA. Inset: Stern–Volmer plot obtained at lower concentration of PA.

However, at a higher concentration of PA, the plot bent upward (Figure 4B), thus indicating superamplified quenching effect.¹⁵ The detection limit was found to be 500 ppb for PA (see Figure S7, Supporting Information). Interestingly, aggregates of derivative **3** are more sensitive toward PA than TNT ($K_{\text{sv}} = 4.3 \times 10^3\ \text{M}^{-1}$, see Figure S8, Supporting Information). We believe that main quenching mechanism for PA is the energy transfer which is a long-range process whereas for TNT main quenching mechanism is short-range charge-transfer process (vide infra).^{15c,16}

This explains the higher sensitivity of aggregates of derivative **3** toward PA than TNT. This assumption is corroborated by presence of a spectral overlap between absorption spectrum of picric acid and emission spectrum of nanoaggregates in the wavelength region of 425–480 nm (see Figure S3, Supporting Information). However, no spectral overlap between absorption of TNT and the emission of aggregates is observed (see Figure S4, Supporting Information). Further, UV–vis spectra of aggregates of derivative **3** in the presence of increasing amounts of TNT (0–100 equiv) show the appearance of tail in the visible region which indicate interaction between aggregates and TNT, thus suggesting charge-transfer between them (see Figure S5, Supporting

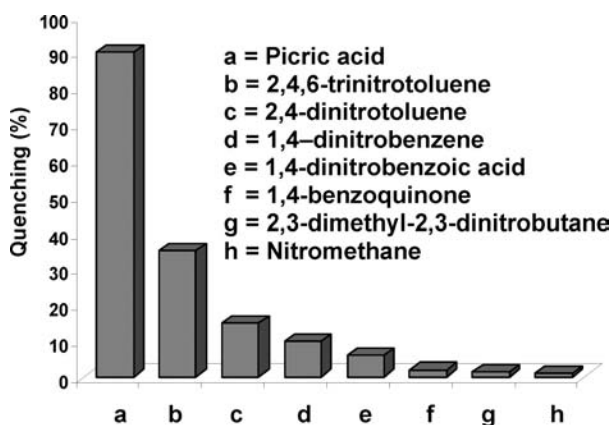


Figure 5. Extent of fluorescence quenching of **3** (10 μ M) observed in H₂O/THF (9:1) mixture after the addition of 35 equiv of various nitro derivatives.

Information).^{15c} The quenching in fluorescence emission of compound **3** in the mixture of H₂O/THF (9:1) was observed with DNT (850 equiv), DNB (1000 equiv), DNBA (1200 equiv), BQ (1500 equiv), NM (> 3000 equiv), and DMDNB (> 3000 equiv) (see Figures S9–S12, Supporting Information). The results of fluorescence studies of compound **3** with PA, TNT, DNT, DNB, DNBA, BQ, NM, and DMDNB are summarized in Figure 5.

We also carried out fluorescence titration of derivative **3** toward picric acid in THF, and the detection limit was found to be 1 μ M for PA (see Figure S6, Supporting Information). Thus, nanoaggregates give a better detection limit. We believe that nanoaggregates of derivative **3** offer more diffusion channels for the excitons to migrate, thus allowing them to be more quickly annihilated by the picric acid.^{15c} This result shows the significance of aggregates in the recognition process.

In addition, picric acid detection was also carried out in the solid state. Compound **3** adsorbed on TLC plate shows strong emission which becomes nonemissive when a spot of PA solution was adsorbed on compound **3** and can be observed by naked eye (Figure 6).

We also prepared test strips by dip-coating solution of compound **3** on Whatman filter paper followed by drying the strips under vacuum. Fluorescence quenching was observed upon dipping the test strips into aqueous solution of PA upon illumination with UV lamp, (Figure 7). This result demonstrates the utility of the test strips for the instant visualization of traces of PA. Although several fluorescent sensors for

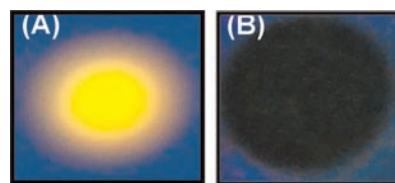


Figure 6. Fluorescence image (under 365 nm UV light) of compound **3** (A) adsorbed on a TLC plate (B) with a spot of PA solution on compound **3**.

nitroderivatives are known,¹⁷ derivative **3** upholds good selectivity for PA over other nitroaromatic compounds.

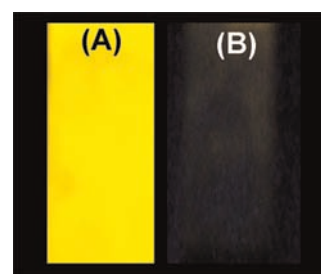


Figure 7. Photographs (under 365 nm UV light) of compound **3** on test strips (A) before and (B) after dipping into aqueous solutions of PA.

In conclusion, we designed and synthesized AIEE-active pentacenequinone derivative **3** using Suzuki–Miyaura coupling. Derivative **3** forms fluorescent organic nanoaggregates in mixed aqueous media and works as efficient and selective fluorescent sensor for nanomolar detection of picric acid in solution as well as in solid state.

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Supporting Information Available. Experimental procedure and characterization data including mp, ¹H, ¹³C and mass spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.