

Self-Assembled Pentacenequinone Derivative for Trace Detection of Picric Acid

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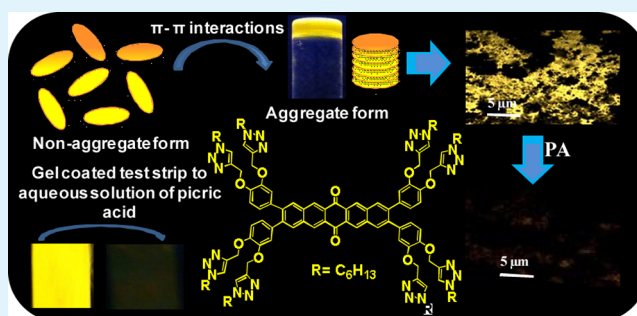
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Supporting Information

ABSTRACT: Pentacenequinone derivative 3 forms luminescent supramolecular aggregates both in bulk as well as in solution phase. In bulk phase at high temperature, long-range stacking of columns leads to formation of stable and ordered columnar mesophase. Further, derivative 3 works as sensitive chemosensor for picric acid (PA) and gel-coated paper strips detect PA at nanomolar level and provide a simple, portable, and low-cost method for detection of PA in aqueous solution, vapor phase, and in contact mode.

KEYWORDS: pentacenequinone, liquid crystal, organogel, supramolecular aggregates, columnar mesophase, chemosensor



INTRODUCTION

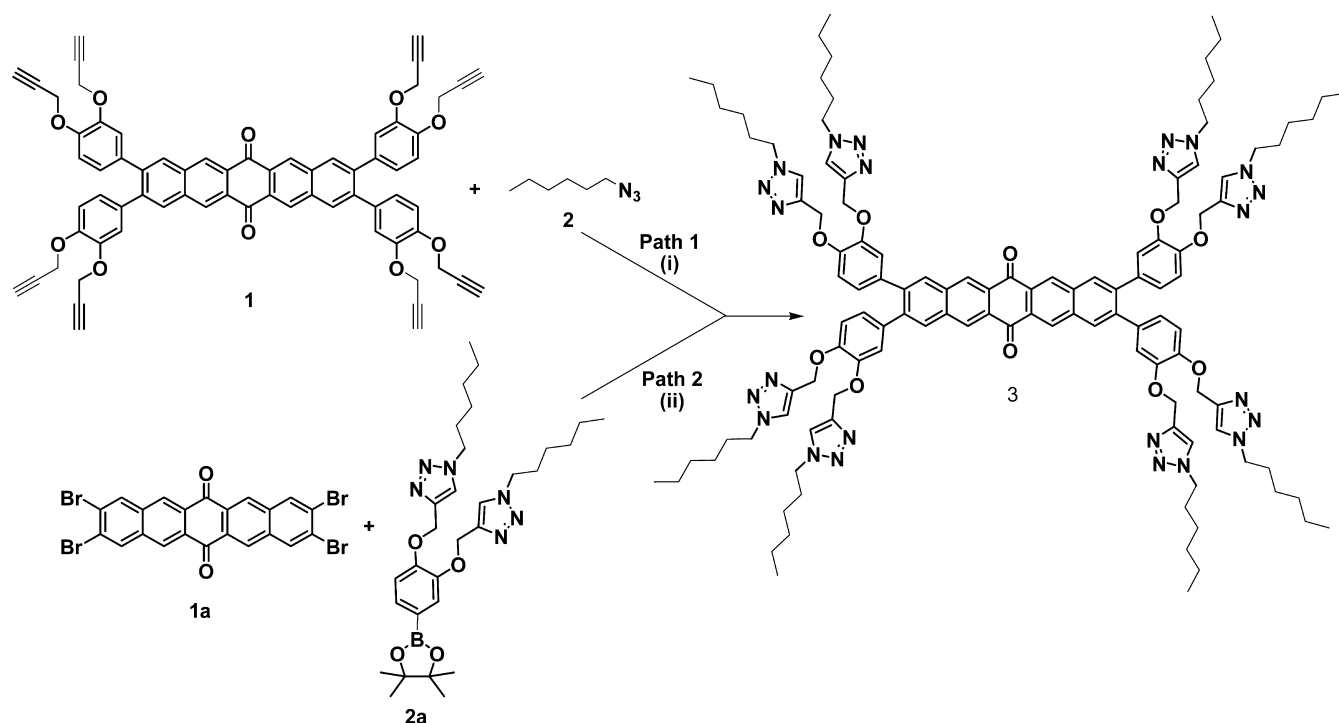
Nitroaromatic compounds (NAC) such as trinitrotoluene (TNT), dinitrotoluene (DNT), and picric acid (PA) are well-known primary constituents of many unexploded land mines worldwide. Further, soil and groundwater of war zone and military facilities can contain toxic levels of these compounds and their degradation products. Thus, these compounds are considered as environmental contaminants and toxic to living organisms.^{1–3} The concern over the adverse effects of nitroaromatics on environment and health provide the sufficient impetus to develop cost efficient, selective, portable, fast, and sensitive method for detection of nitroaromatics.^{4–6} Among various techniques used for the detection of nitroaromatics, fluorescence signaling is one of the first choices because of its high detection sensitivity and selectivity. To date, various fluorescent chemosensors, fluorescent polymers, and nanoparticles have been developed for detection of nitroaromatics.^{7–22} Out of which, fluorescent conjugated polymers are considered to be more advantageous as compared to small fluorescent molecules because of their excellent molar absorptivity, high quantum yields and amplified sensory responses.²³ However, real time monitoring of the polymeric materials is limited because of their multi step conventional covalent synthesis. Recently, several fluorescent nanofibers obtained by molecular self-assembly have been reported as sensing materials for detection of nitroaromatic explosives.^{24,25,26a} Fluorescent molecular assemblies have a large planar surface because of effective π - π stacking between the molecules.²⁵ These fluorescent molecular assemblies are the efficient scaffold for the construction of light harvesting, white light emitting, fluorescence imaging materials and for the

detection of various analytes.²⁷ The one-dimensional π - π stacking provide ordered molecular organization, thus, enabling long-range exciton migration and their quick annihilation by the explosive quenchers. Further, the network formed by interdigitated nanofibers produces multiscale porosity, hence making them an ideal material for sensing of nitroaromatics.^{28–30} In several cases, fluorescent nanofibers have been reported to be good sensing materials for the detection of TNT and DNT.^{24–26} However, detection of PA at ppb level using molecular self-assemblies remains a challenge. Development of quick and sensitive chemosensors for PA is important as it is widely used in the manufacture of rocket fuels and fireworks.^{31,32} Further, explosive power of PA is superior to that of TNT. Recently, from our laboratory, we reported a pentacenequinone derivative that forms fluorescent nanoaggregates in aqueous media that selectively sense picric acid in solution phase.^{33a} But these nanoaggregates could not detect picric acid in vapor phase and contact mode. However, detection of nitroaromatics is essential both in vapor and aqueous phases for security screening, environmental quality monitoring and industrial process controlling.^{33b} Further, moderate vapor pressure of picric acid makes its vapor phase detection more challenging.^{33c} In continuation of this work, we were interested in synthesis of new materials with more defined morphologies for selective and sensitive detection of picric acid in solution, solid and vapor phase. In the present investigation, we designed and synthesized a new pentacenequinone

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Scheme 1. Synthesis of Pentacenequinone-Based Compound 3^a

^aKey: (i) CuI, DMF (Dry), 70–80 °C; (ii) Pd(PPh₃)₄, K₂CO₃ (2 M), 1,4-dioxane, 80–90 °C.

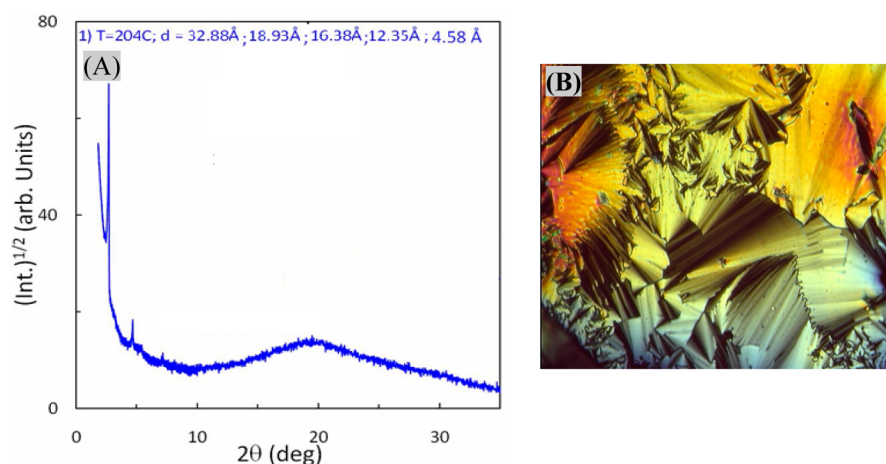


Figure 1. (A) Powder X-ray diffraction pattern of the columnar mesophase of compound 3 at 204 °C. (B) Polarized optical microscopic image of compound 3 at 204 °C.

derivative which forms fluorescent nanofibers which selectively sense picric acid among various nitroaromatics tested. We have chosen pentacenequinone moiety as the motif for preparation of luminescent supramolecular aggregates because of the tendency of 6,13-pentacenequinones to form ordered thin films which make them good candidates for preparation of organic electronic devices.^{34–36} Besides, pentacenequinone derivatives are important precursors for the design and synthesis of solution-processable pentacene derivatives³⁷ but the potential of these derivatives as self-assembling materials is still unexplored. We envisioned that rigid pentacenequinone motif bearing flexible alkyl chains and having 1,2,3-triazole groups as connecting units may form luminescent supramolecular assemblies. Interestingly, pentacenequinone derivative 3 bearing 1,2,3-triazole groups forms supramolecular

aggregates in bulk as well as in solution phase and during the self-assembly in bulk phase formation of stable columnar phase on heating is observed. Interestingly, derivative 3 works as sensitive chemosensor for PA. We also prepared gel-coated paper strips that serve as a simple, portable, fast, and low-cost method for detection of PA in aqueous solution at the parts per billion level. To the best of our knowledge, this is the first report where a pentacenequinone derivative forms supramolecular assemblies both in bulk as well as in solution phase and works as sensitive chemosensor for PA. In addition, the present study shows the transformation of short-range columnar stacking obtained in the bulk phase to long-range columnar stacking, which is of significant interest for the preparation of supramolecular electronic materials.

RESULTS AND DISCUSSION

Pentacenequinone derivative **3** was synthesized by Cu (I) catalyzed “click reaction” of compound **1**³⁸ with hexylazide **2** (Scheme 1, Path 1) in 25% yield. We also prepared compound **3** via Suzuki-Miyaura coupling of 2,3,9,10-tetrabromopentacenequinone **1a** with boronic ester **2a** (see pS4 in the Supporting Information) in 50% yield (Scheme 1, Path 2).

The structure of compound **3** was characterized by ¹H NMR, ¹³C NMR, mass, and elemental analysis. The ¹H NMR spectrum of compound **3** showed nine singlets (4H, 4H, 4H, 4H, 4H, 8H, 8H, 16H, 48H), two doublets (4H, 4H), one triplet (24H) and one multiplet (16H) (see Figure S28 in the Supporting Information). The mass spectrum of compound **3** showed a parent ion peak at *m/z* 2062.317 (M+1)⁺ (see Figure 30 in the Supporting Information). These spectroscopic data corroborate the structure **3** for this compound.

Polarized optical microscopy (POM) analysis and powder X-ray diffraction studies (Figure 1) of derivative **3** show presence of isotropic phase at 233 °C and columnar mesophase in the temperature range 187 to 206 °C. The hexagonal columnar structure is assigned on the basis of ratio 1:0.58:0.5:0.38 for the positions of strong reflections observed in the powder X-ray scans. Further, absence of diffraction peak in the range expected for the π - π stacking corresponding to a distance of 3.5 Å, suggests short-range columnar stacking. Differential scanning calorimetry (DSC) analysis of derivative **3** provided no clear thermal information.

However, interesting results were obtained by gradually cooling isotropic melt of the compound **3** several times. DSC analysis of this sample shows appearance of mesophase at 205 °C and absence of any phase transition in the temperature range 30 to 205 °C (see Figure S2 in the Supporting Information). POM analysis (inset of Figure 2, Figure S3,

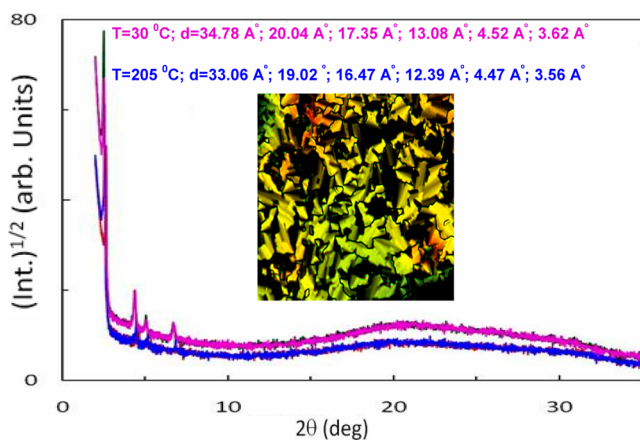


Figure 2. Powder X-ray diffraction pattern of the compound **3** at 30 and 205 °C obtained after reheating and cooling cycle. Inset polarized optical microscopic image of compound **3** at 30 °C.

Supporting Information) and temperature dependent powder X-ray diffraction studies exhibit columnar mesophase which does not change over the temperature range 30 to 205 °C (Figure 2, Figure S1, Supporting Information). The assignment of hexagonal columnar structure is based on the powder X-ray diffraction scans which show the ratio of 1:0.58:0.5:0.38 for the positions of strong reflections. The presence of wide range of columnar mesophase over the temperature range 30 to 205 °C along with the presence of diffraction peak at 3.56 Å, in the

range expected for the π - π stacking indicate long-range columnar stacking after heating and cooling cycles.

We believe that reheating and cooling cycles in bulk phase transform short-range columnar stacking to long-range columnar stacking. Such behavior is rarely observed.³⁹ The above results also demonstrate the thermal stability of the compound at high temperature followed by cooling and reheating cycles.

The gelation ability of derivative **3** in different solvents was confirmed by the “stable-to-inversion protocol of a test tube” method.

It is freely soluble in CH₂Cl₂, CHCl₃ and THF and forms stable opaque gel (see Figure S4 in the Supporting Information) in mixture of toluene/DCM (8:2), benzene/DCM (8:2) and o-xylene/DCM (8:2) and weak gel in p-xylene (see Figure S5A in the Supporting Information). We investigated the gel state for different portions of toluene/DCM and found that optimum portion to form gel state is 8:2 and lowest concentration for the gel formation in this ratio is 1.25 wt %/vol (see Figure S5C in the Supporting Information). The organogels are thermoreversible and stable for several months (Figure 3). The POM image of the organogel of

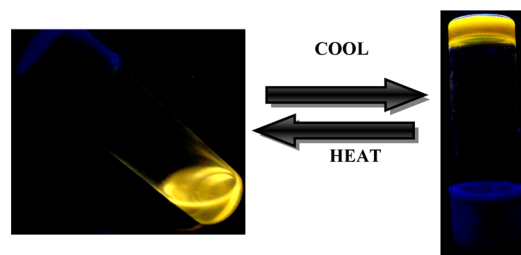


Figure 3. Photographs of gel (under 365 nm UV light) of compound **3** formed in toluene/DCM (8:2) solvent implement sol phase transition by heating–cooling.

compound **3** in toluene/DCM shows birefringence at room temperature (Figure 4A), thus, indicating ordered morphology

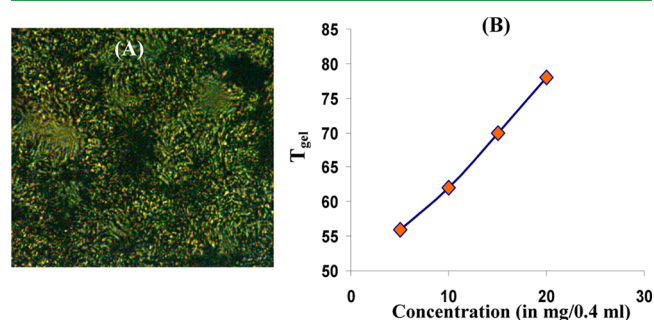


Figure 4. (A) Polarized optical microscope image gelator **3** formed in toluene/DCM at room temperature through crossed polarizing filters. (B) Variation of T_{gel} with increasing concentration of the gelator **3** in toluene/DCM (8:2).

in solution phase. Thermal stability of the gel was measured by the dropping ball method.^{40a} The sol–gel transition temperature (T_{gel}), the required temperature for the organogel to collapse, increases with increase in concentration of gelator as is clear from the plot of the gel to sol melting temperature, T_{gel} , against the concentration of compound **3** (Figure 4B). At concentration $\geq 6.25\%$ wt/vol precipitation takes place (see Figure S5B in the Supporting Information).

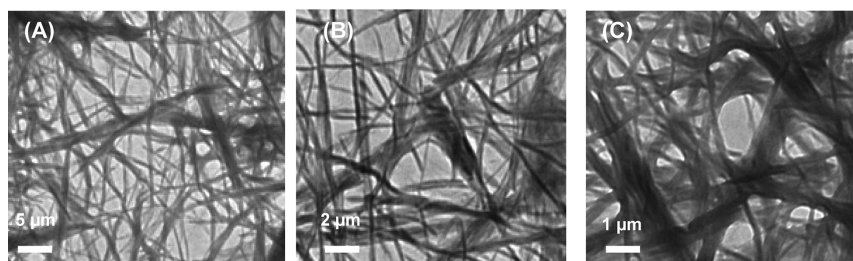
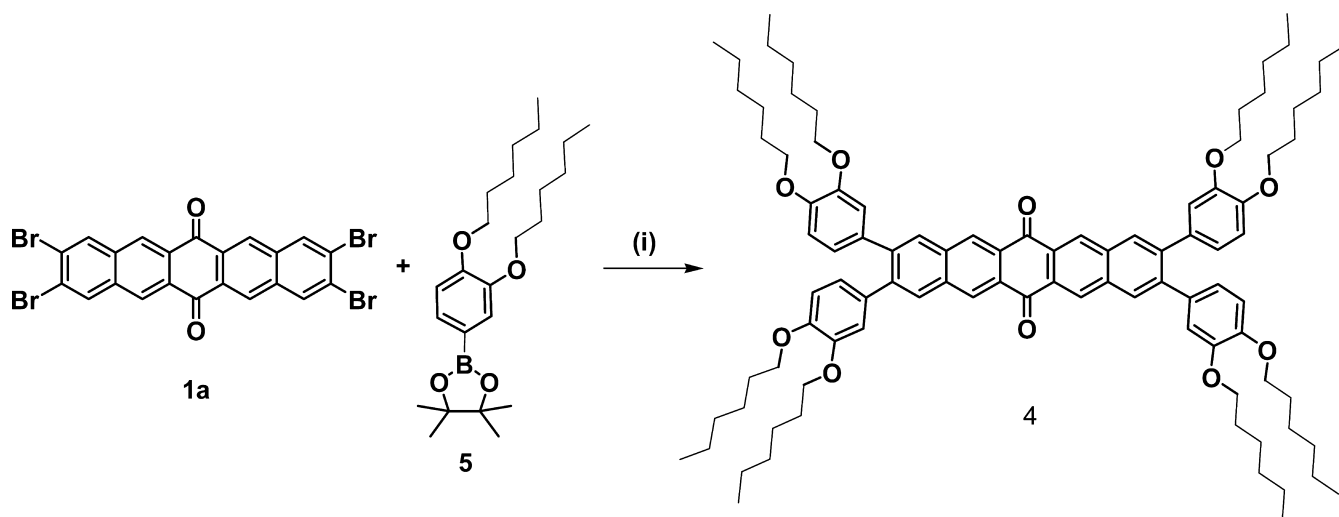


Figure 5. TEM images of toluene/DCM organogelator 3 scale bar (A) 5, (B) 2, and (C) 1 μm .

Scheme 2. Synthesis of Pentacenequinone-Based Compound 4^a



^aKey: (i) $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 (2 M), 1,4-dioxane, 80–90 $^\circ\text{C}$.

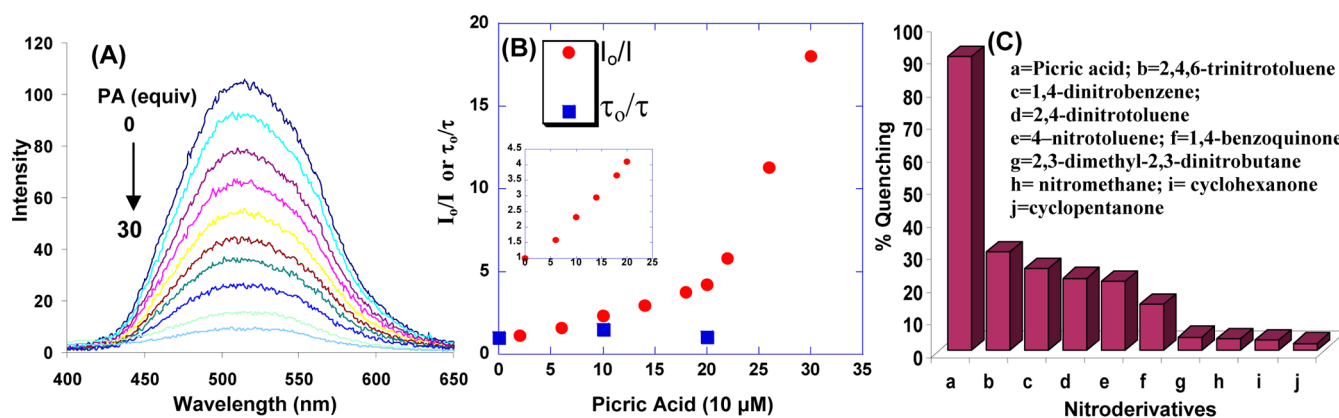


Figure 6. (A) Change in the fluorescence spectra of compound 3 (10 μM) with the addition of PA in toluene/DCM (8:2) solution, $\lambda_{\text{ex}} = 330 \text{ nm}$ (B) Stern–Volmer plot in response to PA and inset figure shows the Stern–Volmer plot obtained below 200 μM concentration of PA. (C) Comparison of fluorescence quenching of 3 (10 μM) in toluene/DCM (8:2) after the addition of 30 equiv of various nitroderivatives.

The gel stability is qualitatively in agreement with the morphology exhibited by transmission electron microscopy (TEM) studies. The TEM images of compound 3 showed the presence of numerous fibers entangled with one another to give the extended fibrillar network structure, thus indicating tendency of the molecule to self-assemble into 1D fibers (Figure 5). We believe that in addition to effective π – π stacking between pentacenequinone molecules the extended fibrillar network structure of compound 3 could result from the hydrophobic interactions between flexible alkyl chains attached

to triazole rings.^{40b} This extended network of interlocked fibers is responsible for the immobilization of the solvent and gel formation. Further, the more entangled fiber morphology observed in gel of compound 3 indicates stronger interactions between individual fibers.

We also prepared a model compound 4⁴¹ without 1,2,3-triazole groups (Scheme 2) that exhibits liquid crystalline behavior but displays no gelation abilities, thus suggesting that dipole–dipole and π – π interactions between 1,2,3-triazoles played a synergic effect in formation of the gel.

We believe that π - π interactions between the pentacenequinone molecules are responsible for columnar assembly. In addition, the presence of lone-pair electrons on heteroatoms in 1,2,3-triazole groups introduces a transverse dipole moment⁴² and triazole groups forms a pseudo network by their dipole-dipole and π - π interactions,^{43a} which stabilizes the columnar assembly of pentacenequinone moiety.

To investigate the mode of aggregation in compound 3, we carried out absorption studies of 3 in different ratios of DCM and toluene (starting from pure DCM to pure toluene) at fixed concentration of 3. It was observed that with increasing toluene fraction there was blue shift (5 nm) of the absorption band from 360 to 355 nm which indicates the formation of H-aggregates. Further, compound 3 in toluene/DCM (8:2) mixture exhibited a multiexponential character with significant longer lifetime (0.12, 0.60, and 1.84 ns) as compared to solution in DCM (0.11, 0.45, and 0.47 ns) which confirms the presence of static excimers^{43b,c} formed from H-type organization⁴⁴ (see Figure S7 in the Supporting Information).

In the next part of our investigation, we carried out fluorescence studies of compound 3 with picric acid, 2,4,6-trinitrotoluene (TNT), 1,4-dinitrotoluene (DNT), 2,4-dinitrobenzene (DNB), 4-nitrotoluene (NT), 1,4-benzoquinone (BQ), 2,3-dimethyl-2,3-dinitrobutane (DMDB), nitromethane (NM), cyclohexanone and cyclopentanone. Among various nitro derivatives tested, compound 3 showed sensitivity toward PA. Upon addition of 30 equiv of picric acid, the emission band of 3 (1.0×10^{-5} M) at 515 nm in toluene/DCM (8:2) is completely quenched (Figure 6A). A linear Stern–Volmer plot was obtained from fluorescence quenching titration (inset of Figure 6B) when concentration of PA is below 200 μ M. However, at a higher concentration of PA, the plot bent upward (Figure 4B), thus, indicating superamplified quenching effect.^{22c,45} The estimated Stern–Volmer constant for picric acid is 1.55×10^4 M⁻¹ which is found to be higher as compared to other reported chemosensors for picric acid.^{17,18,46a–c} The detection limit was found to be 3.5×10^{-7} M. To get insight into the detection mechanism, we measured fluorescence lifetime of derivative 3 in the absence and presence of PA. The fluorescence lifetime of compound 3 is found to be invariant at different concentration of PA (see Figure S8 in the Supporting Information) thus, indicating that the quenching is static in nature and ground state complex is formed between compound 3 and PA. Further, the UV–vis absorption studies of derivative 3 with PA show the appearance of new band at 450 nm with formation of level-off tail in the visible region which indicates interaction between derivative 3 and PA, thus, suggesting charge-transfer between them (see Figure S9 in the Supporting Information).^{22c} We carried out blank UV–vis titration with PA only as control experiment under similar set of conditions as used for 3 with PA, no band at 450 nm with any level-off tail was observed (see Figure S10 in the Supporting Information). Thus, appearance of new band at 450 nm and formation of level-off tail in the visible region with the addition of PA to solution of derivative 3 indicates charge-transfer between them. Further, we carried out the fluorescence titration of compound 3 with addition of 30 equiv. of PA at various excitation wavelengths (310, 315, 320, 325, 330, 335, 340, 345, 350, 355, 360, 365, and 370 nm). No significant change in quenching efficiency of PA was observed (see Figure S11 in the Supporting Information). These results ruled out the possibility of decrease in fluorescence intensity of 3 due to masking by PA.

The quenching in fluorescence emission of compound 3 in the mixture of toluene/DCM (8:2) was observed with TNT (210 equiv), DNB (250 equiv), DNT (350 equiv), NT (800 equiv), BQ (1300 equiv), NM (>3000 equiv), DMDB (>3000 equiv), cyclohexanone (>5000 equiv) and cyclopentanone (>5000 equiv) (see Figure S13 in the Supporting Information). The results of fluorescence studies of compound 3 in toluene/DCM with various nitro derivatives are summarized in Figure 6C and it is evident that the most electron-deficient aromatic substrates engendered the greatest quenching, i.e., the greater the number of electron-withdrawing nitro ($-\text{NO}_2$) groups present on benzene/toluene core, the more extensive the degree of fluorescence quenching. This finding is consistent with the proposed mechanism, in which nitroaromatic analyte acts as fluorescence quencher as the result of an electron-transfer event. Cyclic voltammetry studies of derivative 3 (see Figure S12 in the Supporting Information) also confirm the electron-transfer event as the higher energy lowest unoccupied molecular orbital (LUMO, -3.0 eV) of the compound 3 facilitates the electron to jump to the lower energy LUMO of PA (-3.89 eV).^{47a} The LUMO energy level of PA is lower than TNT (-3.7 eV),¹⁸ DNT (-3.5 eV),⁹ NT (-3.2 eV)⁹ and DMDB (-2.7 eV)⁴⁸ etc. Thus, there seems to be a relationship between sensitivity and LUMO energy level of the analytes. Further, we believe that high polarizability of PA could be another factor for its high quenching response toward 3 over other nitroaromatics.⁴⁷

During manufacturing of rocket fuel and fire works, PA can contaminate the human body, clothing and other materials in the surroundings. In this context, checking of residual contamination in contact mode is appropriate. Thus, we prepared test strips by dip-coating hot solution of gel on Whatman filter paper followed by drying the strips under vacuum. The SEM image of the filter paper before coating with the gel shows micrometer sized filter paper fibers. However, filter paper fibers are completely covered by the entangled fibers of the assembled molecule of derivative 3 as shown by SEM image of gel-coated filter paper (see Figure S14 in the Supporting Information). We prepared several samples of gel coated filter papers and studied the response of their fluorescence toward picric acid in contact mode and solution phase. PA crystals were placed over a test strip for 5 s to test the contact mode response of gel fibers of derivative 3 toward PA. Upon illumination with UV lamp, black spots were observed in the contact area (Figure 7).

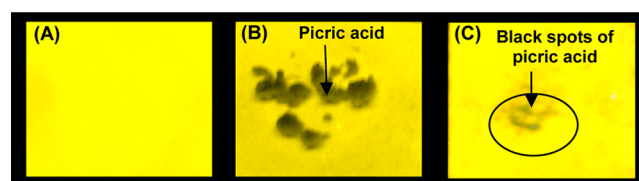


Figure 7. Photographs (under 365 nm UV light) of organogel of compound 3 on test strips (A) test strip (B) picric acid crystal on test strip and (C) upon removal of picric acid crystals after 5 s.

Further, fluorescence quenching was observed upon dipping the test strips into saturated aqueous solution of PA. However, revival in the fluorescence was observed after washing the test strip with water (see Figure S18A in the Supporting Information). For detection of very small amounts of PA, we

prepared the aqueous solution of PA of different concentration and 6 μL of each solution was placed on gel coated test strip.

The visual detection response of PA at different concentration is shown in Figure 8. The minimum amount of PA, detectable by naked eye was up to ppb level.

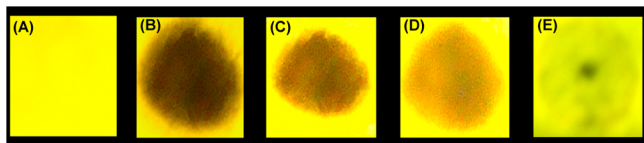


Figure 8. Photographs (under 365 nm UV light) of fluorescence quenching of organogel of compound 3 on test strips for the visual detection of small amount of PA (A) test strip; PA of different concentrations (B) 1×10^{-3} M, (C) 1×10^{-5} M, (D) 1×10^{-7} M, and (E) 1×10^{-9} M.

We also prepared test strips by dipping the filter paper in toluene solution of derivative 3. However, minimum amount of PA, detectable by naked eye using these strips was up to ppm level (see Figure S15 in the Supporting Information). SEM image of solution coated paper strip (see Figure S14 in the Supporting Information) indicates partial covering of filter paper fibers by molecules of derivative 3, thus, lower detection limit is observed in case of solution coated filter paper strips. We believe that effective π - π stacking between pentacenequinone molecules provides highly porous structure and allow PA molecules to penetrate into porous network, thus efficiently amplify the sensing signal for the detection of PA.⁴⁹ These results demonstrate the utility of the gel-coated test strips for the instant visualization of traces of PA. For vapor detection of PA, we exposed gel-coated glass slide to vapors of PA by inserting it into sealed vial at room temperature containing solid PA and emission spectra were measured using a front-face technique after exposing the film for specific interval. Nearly 15% quenching of emission intensity was observed within 2 min and 20% quenching was observed within 5 min (Figure S16, Supporting Information). To get insight in to the excited-state behavior, the fluorescence lifetime decay of gel-coated glass slide (0.17, 0.87, and 1.94 ns) before and after exposure to PA vapors was recorded and found to be invariant (see Figure S17 in the Supporting Information). This result suggests electrostatic interaction between PA and organogel.⁴⁹ Further, absorption spectra of the gel-coated glass slide before and after exposure to PA vapors shows the appearance of band at 485 nm with level-off tail in the visible region support the formation of ground-state complex between PA and organogel (see Figure S18B in the Supporting Information).^{22c} Confocal images of gel-coated glass slide before and after dipping in aqueous solution of PA are shown in Figure 9.

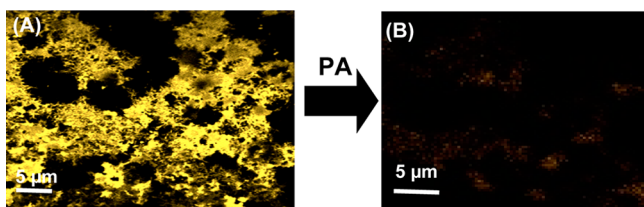


Figure 9. Confocal images of gel-coated glass slide (A) before and (B) after dipping in aqueous solution of PA. $\lambda_{\text{ex}} = 405$ nm.

CONCLUSION

A novel pentacenequinone derivative 3 has been designed and synthesized which forms supramolecular aggregates both in bulk as well as in solution phase. In bulk phase at high temperature, long-range stacking of columns is observed which leads to formation of stable and ordered columnar mesophase. Derivative 3 serves as a sensitive chemosensor for picric acid and gel-coated paper strips serve as a simple, portable, sensitive, fast, and low-cost method for detection of PA at the parts per billion level.

EXPERIMENTAL SECTION

General Experimental Procedures. All reagents were purchased from Aldrich and were used without further purification. UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length, 1 cm). The cell holder was thermostatted at 25 °C. The fluorescence spectra were recorded with a SHIMADZU 5301 PC spectrofluorimeter. The time resolve fluorescence spectra were recorded with a Time Resolve Fluorescence Spectrometer (TRFS)-Edinburgh FL 920. Differential scanning calorimetry (DSC) was recorded on a Perkin-Elmer DSC7. The TEM images were recorded from Transmission Electron Microscope (TEM) - JEOL 2100F. The SEM images were recorded from Scanning Electron Microscope (SEM)-ZeissEV040. The Confocal images were taken from Laser Confocal Microscope with Fluorescence Correlation Spectroscopy (FCS)-Olympus FluoView FV1000. Polarized optical microscope (POM) images were recorded on NIKON ECLIPSE LV100 POL. Elemental analysis (C, H, N) was performed on a Flash EA 1112 CHNS-O analyzer (Thermo Electron Corp.). ¹H NMR was recorded on a JEOL-FT NMR-AL 300 MHz spectrophotometer using CDCl₃ as solvent and tetramethylsilane SiMe₄ as internal standards. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, br = broad singlet m = multiplet), coupling constants J (Hz), integration, and interpretation. Silica gel 60 (60–120 mesh) was used for column chromatography.

4-Bromo-1,2-bis(prop-2-ynyloxy)benzene (2b). To a solution of 4-bromocatechol (2.5 g, 13.22 mmol) in dry DMF (15 mL) was added K₂CO₃ (7.3 g, 52.9 mmol), and mixture was stirred at room temperature for 10–15 min. Then propargyl bromide (6.2 g, 52.9 mmol) was added dropwise and slowly with continues stirring the reaction mixture. The resulting mixture was heated at 60–70 °C overnight. After the completion of reaction (TLC), the mixture was then diluted with DCM and washed with water. The organic layer was separated, dried over Na₂SO₄ and the solvent was evaporated under reduce pressure to get the crude. The crude product was purified from column chromatography, eluting with mixture of hexane/chloroform (9:1) to give compound to yield 2b as white amorphous solid in (2.457 g) 70% yield. MP 80–90 °C. ¹H NMR δ (300 MHz, CDCl₃): 2.51 (t, 1H, J = 2.4 Hz), 2.55 (t, 1H, J=2.25 Hz), 4.73 (t, 4H, J = 2.85 Hz), 6.92 (d, 1H, J = 8.4 Hz), 7.09 (d, 1H, J = 8.7 Hz), 7.17 (s, 1H). ¹³C NMR δ (75.45 MHz, CDCl₃): 57.0, 76.1, 78.0, 114.0, 116.3, 118.1, 124.7, 146.7, 148.2. MS ESI *m/z*: 265.3 (M+1)⁺. Elemental anal. Calcd for C₁₂H₉BrO₂: C, 54.37; H, 3.42. Found: C, 54.21; H, 3.33.

4-((2-((1-Hexyl-1H-1,2,3-triazol-4-yl)methoxy)-4-bromophenoxy)methyl)-1-hexyl-1H-1,2,3-triazole (2c). To the mixture of 2b (2 g, 7.54 mmol) and hexylazide (3.83 g, 30.18 mmol) in dry DMF was added Cu(I) (0.716 g, 3.77 mmol). The reaction mixture was heated at 90 °C overnight under nitrogen. The mixture was diluted with water and extracted with DCM. The organic layer was separated out, dried over anhydrous Na₂SO₄ and concentrated under vacuum to get the crude which was purified by column chromatography, eluting with mixture of hexane/ethyl acetate (6:4) to get the click compound 2c as white amorphous solid in (2.355 g) 60% yield. MP 70–80 °C. ¹H NMR δ (300 MHz, CDCl₃): 0.87 (t, 6 H, J = 6.1 Hz), 1.30 (s, 12 H), 1.88 (s, 4 H), 4.36–4.29 (m, 4 H), 5.22 (s, 4H), 6.90 (d, 1 H, J = 8.7 Hz), 7.02 (d, 1 H, J = 8.7 Hz), 7.14 (s, 1H), 7.63 (s, 1H), 7.64 (s,1H). ¹³C NMR δ (75.45 MHz, CDCl₃): 13.6, 22.0, 25.7, 29.8, 30.7, 50.0, 63.3, 113.5, 116.6, 118.4, 122.8, 124.4,

142.9, 143.1, 147.4, 149.0. MS ESI m/z : 519.2 (M+1)⁺. Elemental anal. Calcd for C₂₄H₃₅BrN₆O₂: C, 55.49; H, 6.79; N, 16.18. Found: C, 55.37; H, 6.70; N, 16.11.

4-((2-((1-Hexyl-1H-1,2,3-triazol-4-yl)methoxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)methyl)-1-hexyl-1H-1,2,3-triazole (2a). To a suspension of [PdCl₂(PPh₃)₂] (0.108 g, 0.154 mmol) in 1,4-dioxane (15 mL) were added **2c** (2.0 g, 3.85 mmol), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.47 g, 11.56 mmol), and triethylamine (1.67 g, 11.56 mmol) under a nitrogen atmosphere. After stirring for 5 h at 80 °C, the dioxane was removed under vacuum and the residue so obtained was treated with water, extracted with dichloromethane, and dried over anhydrous Na₂SO₄. The organic layer was evaporated and the compound was purified by column chromatography eluting with mixture of hexane/ethylacetate (6:4) to give compound **2a** as gum in (1.639 g) 75% yields. ¹H NMR δ (300 MHz, CDCl₃): 0.85 (t, 6 H, 6.45 Hz), 1.30 (s, 12 H), 1.33 (s, 12H), 1.89 (s, 4 H), 4.36–4.28 (m, 4 H), 5.22 (s, 4H), 6.91 (d, 1 H, J = 8.7 Hz), 7.02 (d, 1 H, J = 8.4 Hz), 7.14 (s, 1H), 7.65 (s, 1H), 7.66 (s, 1H). ¹³C NMR δ (75.45 MHz, CDCl₃): 13.8, 22.3, 24.5, 24.7, 26.0, 30.1, 31.0, 50.3, 63.5, 83.6, 118.5, 122.8, 124.6, 129.5, 144.0, 151.1. MS ESI m/z : 567.34 (M+1)⁺. Elemental anal. Calcd for C₃₀H₄₇BN₆O₄: C, 63.60; H, 8.36; B, 1.91; N, 14.83. Found: C, 63.55; H, 8.34; N, 14.75.

2,3,9,10-Tetrakis(3,4-bis((1-hexyl-1H-1,2,3-triazol-4-yl)methoxy)phenyl)pentacene-6,13-dione (3), Path 1. To the mixture of **1** (0.5 g, 0.478 mmol) and **2** (0.728 g, 5.736 mmol) in dry DMF was added Cu(I) (0.045 g, 0.239 mmol) under a nitrogen atmosphere. The reaction mixture was heated at 70–80 °C overnight. After completion of the reaction (TLC), the flask was allowed to cool to room temperature. The mixture was diluted with water and extracted with DCM. The organic layer was separated out, dried over anhydrous Na₂SO₄ and concentrated under vacuum to get the crude which was purified by column chromatography, eluting with mixture (9:1 Chloroform/Methanol) provided the product **3** as yellow amorphous solid in (0.415 g) 25% yield. ¹H NMR δ (300 MHz, CDCl₃): 0.88 (t, 24 H, J = 4.65 Hz), 1.32 (s, 48H), 1.91 (s, 16H), 4.37–4.29 (m, 16H), 4.96 (s, 8H), 5.26 (s, 8H), 6.85 (s, 4H), 6.95 (d, 4 H, J = 8.7 Hz), 7.05 (d, 4 H, J = 8.4 Hz), 7.67 (s, 4H), 7.73 (s, 4H), 8.12 (s, 4H), 8.97 (s, 4H). ¹³C NMR δ (75.45 MHz, CDCl₃): 13.9, 22.4, 26.1, 30.2, 31.1, 50.3, 63.6, 115.0, 117.2, 123.0, 123.0, 123.6, 129.5, 131.0, 134.5, 142.0, 142.2, 143.7, 143.8, 148.0, 172.7. MS (MALDI) m/z : 2062.317 (M+1)⁺. Elemental anal. Calcd for C₁₁₈H₁₄₈N₂₄O₁₀: C, 68.71; H, 7.23; N, 16.30. Found: C, 68.66; H, 7.28; N, 16.20.

2,3,9,10-Tetrakis(3,4-bis((1-hexyl-1H-1,2,3-triazol-4-yl)methoxy)phenyl)pentacene-6,13-dione (3), Path 2. To a mixture of 2,3,9,10-tetrabromopentacenequinone **1a** (0.490 g, 0.785 mmol) and [Pd(PPh₃)₄] (0.200 g, 0.172 mmol) in 1,4-dioxane (20 mL) was added a suspension of **2a** (2 g, 3.53 mmol) in 1,4-dioxane (5.0 mL) and 2 M aqueous solution of K₂CO₃ (0.866 g, 6.28 mmol). The mixture was degassed and purged with N₂ for 15 min. The mixture was refluxed overnight. After completion of the reaction (TLC), the flask was allowed to cool to room temperature. The mixture was extracted with CH₂Cl₂, and the organic layer was washed with brine, dried over Na₂SO₄, and filtered. The filtrate was evaporated to dryness under reduced pressure. Flash chromatography over silica gel (9:1 chloroform/methanol) provided the coupled product **3** as yellow amorphous solid in (0.830 g) 50% yield.

2,3,9,10-Tetrakis(3,4-bis(hexyloxy)phenyl)pentacene-6,13-dione (4). To a mixture of 2,3,9,10-tetrabromopentacenequinone **1a** (0.5 g, 0.80 mmol) and [Pd(PPh₃)₄] (0.203 g, 0.176 mmol) in 1,4-dioxane (20 mL) was added a suspension of **5^{SO}** (1.36 g, 3.36 mmol) in 1,4-dioxane (5.0 mL) and 2 M aqueous solution of K₂CO₃ (0.883 g, 6.4 mmol). The mixture was degassed and purged with N₂ for 15 min. The mixture was refluxed overnight. After completion of the reaction (TLC), the flask was allowed to cool to room temperature. The mixture was extracted with CH₂Cl₂, and the organic layer was washed with brine, dried over Na₂SO₄, and filtered. The filtrate was evaporated to dryness under reduced pressure. Flash chromatography over silica gel (1:1 hexane/chloroform) provided the coupled product **4** as yellow amorphous solid in (0.398 g) 35% yield. ¹H NMR δ (300 MHz,

CDCl₃): 0.89–0.95 (m, 24 H), 1.33–1.38 (m, 48 H), 1.65–1.74 (m, 8 H), 1.79–1.88 (m, 8 H), 3.74 (t, 8H, J = 6.6 Hz), 4.00 (t, 8H, J = 6.6 Hz), 6.71 (s, 4H), 6.83–6.90 (m, 8H), 8.14 (s, 4H), 8.97 (s, 4H). ¹³C NMR δ (75.45 MHz, CDCl₃): 14.0, 22.6, 25.6, 29.0, 31.6, 69.1, 113.2, 115.7, 122.1, 129.4, 130.7, 130.9, 133.1, 134.3, 142.8, 148.5, 148.6, 182.8. MS (ESI) m/z : 1436.9 (M+Na)⁺. Elemental anal. Calcd for C₉₄H₁₂₄O₁₀: C, 79.85; H, 8.84. Found: C, 79.79; H, 8.75.

■ ASSOCIATED CONTENT

Supporting Information

Characterization data including melting point and ¹H, ¹³C, and mass spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

[§]Responsible for powder X-ray diffraction studies.

Notes

The authors declare no competing financial interest.

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