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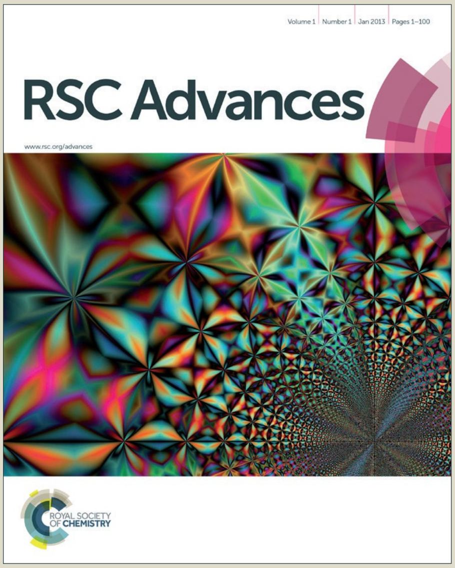

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Electron-rich π-extended phthalocyanine-thiophene-phthalocyanine triad for the sensitive and selective detection of picric acid

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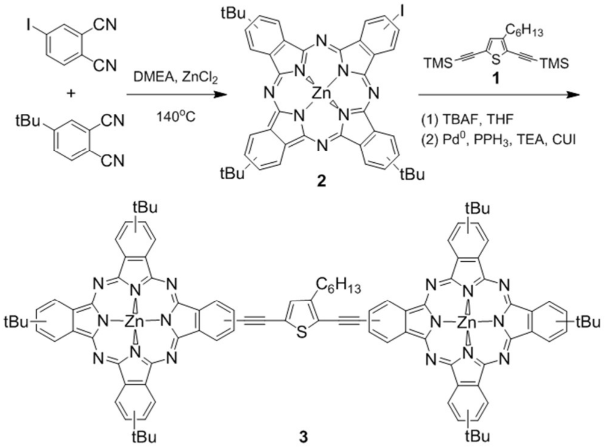
Electron-rich phthalocyanine-thiophene-phthalocyanine triad 3 (Pc-triad 3), newly synthesized, can function as a highly selective chemosensor against picric acid (PA). Pc-triad 3 showed efficient and selective fluorescence quenching towards PA, during which photo-induced electron transfer (PET) complex arose from electron-rich pendant Pc rings of 3 to PA reagents.

During the past decade, the fast and reliable detection of trace nitroaromatic compounds [1] has attracted much attention as these compounds are commonly used in military, security and industrial fields due to their wide range of applications, from explosives to intermediates of dyes.[2] Among the various nitroaromatic compounds currently available, 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), and picric acid (PA) are common high explosives. However, the explosive power of PA is even stronger than that of TNT, and it was widely used as an explosive until World War I.[3] In addition, PA can have serious health effects, as it is considered to be a strong irritant of the skin and eyes and can cause damage to organs involved in the respiratory system.[4] Furthermore, PA, used in the manufacturing of rocket fuel, fireworks, and matches, is released in large quantities into the environment.[5] Hence, for security and environmental protection reasons, the development of efficient sensors to detect PA at very low concentrations is a very appealing field of research.

Various methods have been used for the highly sensitive detection of nitroaromatic explosives; however, these methods require bulky equipment, time-consuming procedures, and complicated manipulation processes. In view of this, fluorescence-quenching-based chemical detection has been widely considered as a more convenient and cost-effective approach. Its main working mechanism is an electron transfer from the electron-rich fluorophore to electron-deficient nitro compounds to result in fluorescence quenching.[6] Further, to attain high detection sensitivity, it is important for the target analytes to be enriched around the surface of the fluorescent sensory materials *via* physical adsorption or chemical interaction, as the fluorescence quenching efficiency is usually dependent on the adsorptive affinity of the sensors to nitroaromatic molecules.[7]

Thus, in view of the above requirements, here we synthesized the phthalocyanine (Pc) based triad **3** for the detection of nitro aromatics. We chose Pc as a core moiety as it exhibits interesting properties which are useful in various applications, such as optical storage, electrophotography, photovoltaic cells, and sensing devices, mainly due to their high stability, architectural flexibility, and diverse coordination properties.[8] In addition, Pcs as an extended electron-rich aromatic structure give rise to high extinction coefficients in the long-wavelength regions. These unique features have prompted intense interest in the use of Pcs in several promising fields based on their excellent spectroscopic characteristics. In spite of several fascinating reports thus far, the interaction of Pcs with NACs has not yet been reported in the literature. Previous reports from our laboratory detailed the highly efficient chemosensory material phthalocyanine against PA.[9] In a continuation of this work, to enhance the sensing sensitivity for PA we designed and synthesized



Scheme 1. Synthetic procedures of Pc-triad **3**.

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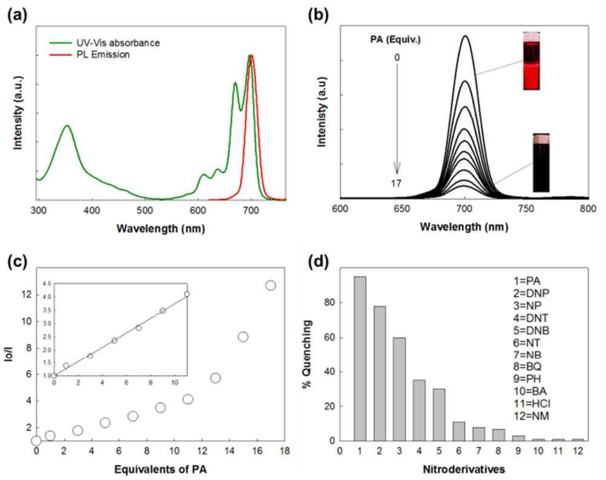


Fig. 1. (a) UV-vis (green) and PL (orange) spectra of **3**. (b) Fluorescence spectra of **3** (10 µM) with the addition of PA. inset: Photograph (under 365 nm UV light) with and without addition of 17 equivalents of PA. (c) Stern-Volmer plot of **3** in response to PA; the inset is a linear plot with PA at less than 100 µM. (d) Bar diagram of **3** after the addition of 17 equivalents of various nitro derivatives in THF:water (6:4).

π-extended Pc-thiophene-Pc triad **3** (Pc-triad **3** hereafter). Our strategy to design a new Pc derivative for sensing nitroaromatic is very simple. First, we increased the conjugation of Pc, as it is known that enlarging the effective conjugation degree of a π-system is an effective way to enhance its performance in sensing an analyte.[10] Further, a bulky *t*-butyl substituent is attached onto the peripheral of the Pc to prevent the formation of an intermolecular excimer through π-π interaction. Thus, herein, we used π-extended Pc-triad **3** for selective and sensitive fluorescence quenching-based sensors for the detection of nitroaromatic explosives. Fluorescence quenching titration revealed that PA showed the largest quenching response with high selectivity among a range of other electron-deficient aromatic compounds.

The synthesis of Pc-triad **3** involves the reaction of thiophene derivative **1** with tetrabutylammonium fluoride (TBAF) in dry THF and its subsequent reaction with mono-iodo Pc **2** using a catalytic amount of bis(triphenylphosphane)palladium(II) chloride, copper(I) iodide and triphenylphosphine (PPh_3) in the presence of triethylamine (Scheme 1). The structure of Pc-triad **3** was confirmed by MALDI mass measurement (See Fig. S1 in ESI†). However, its ^{1}H-NMR spectra revealed no informative data from broadening and overlap of the aromatic signals (Fig. S2), which may be attributed to either extended conjugation or the existence of more than one isomers (from the position of t-Bu).[11]

Pc-triad **3** showed well-defined UV–vis spectra, with sharp Q-bands at 590-710 nm indicative of monomeric species in the solution (Fig. 1a). While no significant features were observed in the B-bands, its Q-band showed maximum absorption at 690 nm with a shoulder at 660 nm. According to a previous report, the splitting of the Q-band was attributed to extended π-conjugation *via* intramolecular electronic coupling between the phthalocyanine subunits. In a fluorescence emission spectrum collected at an excitation at 350 nm, Pc-triad **3** exhibited a mirroring of the Q-band, with a strong fluorescence emission band at 694 nm.

To evaluate the sensing ability of the designed Pc-triad **3** for the detection of nitroaromatic explosives, we initially performed fluorescence quenching titration experiments against PA. Pc-triad **3**, when dissolved in a THF:water (6:4) mixture, exhibited a strong fluorescence emission band at 700 nm upon excitation at 352 nm (Fig. 1b). However, with a gradual addition of nitro aromatics to a solution of **3**, the initial fluorescence intensity was efficiently quenched. This decrease in the fluorescence emission could be readily observed under illumination of 365 nm (Fig. 1b inset). A linear Stern-Volmer plot was obtained from fluorescence quenching titration with PA when its concentration was less than 110 µM, and the Stern-Volmer binding constant (K_{sv}) was calculated to be 2.82 × 10^4 M^{-1} for PA. When the concentration of PA exceeded 110 µM, the plot moved upward (Fig. 1c). This non-linear nature of the plot indicates self-absorption, a combination of static and dynamic quenching, or an energy transfer process between PA and **3**.[12] In order to compare the sensing ability, the fluorescence titration of **3** was also conducted with various nitro-aromatic derivatives, such as 2,4-dinitrophenol (DNP), 4-nitrophenol (NP), DNT, 1,4-dinitrobenzene (DNB), 4-nitrotoluene (NT), nitrobenzene (NB), 1,4-benzoquinone (BQ), phenol (PH), benzoic acid (BA), hydrochloric acid (HCl) and nitromethane (NM). Quenching in the fluorescence of triad **3** was also observed with DNP. However, the Stern-Volmer constant, K_{SV}, for DNP was calculated to be 7.82 x 10^3 M^{-1}, which was very less than that of PA, thus, distinguishing DNP from PA. The detection limit for PA was calculated to be 7.0 × 10^{-7} M (See Fig S6 in ESI†). Obviously, the most electron-deficient aromatic compound caused the greatest degree of quenching. The results of the fluorescence studies of **3** with various nitro derivatives are shown in Fig. 1d.

The aggregational structure of Pc derivative **3** before and after exposure to PA was investigated by XRD analysis. As shown in Fig. 2a (upper in black), its pristine XRD diagram showed two strong diffraction peaks at 2θ = 10.12^o and 20.30^o, which correspond to 0.874 nm and 0.437 nm, respectively. According to the X-ray diffraction analysis of analogous phthalocyanine,[13] the *d*-spacings corresponding to 0.874 nm originated from diffractions at the (002) planes, which could be attributed to the fact that there exists a very regular repetition of the nanostructure and one-dimensionally favorable growing orientation along the long axis of Pc-triad **3**. Further, the *d*-spacing corresponding to 0.437 nm can be attributed to the π-π stacking distance of the phthalocyanine rings. After exposed to PA, however, **3** revealed a major change in its XRD diffraction pattern (Fig. 2a, lower in red). In the wide-angle region, the XRD pattern of the **3** nanostructures present additional diffractions at 0.383 nm; this decrease in the *d*-spacing (0.437 to 0.383 nm) could be attributed to the π-π stacking distance of phthalocyanine and PA. This observation implies that the Pc molecules underwent significant changes in their intermolecular interactions after the addition of the PA molecules.

The IR spectrum of Pc derivative **3** showed an absorption band at 1588 cm^{-1} which was attributed to the C=C stretching of its phenyl ring. However, the IR spectrum of Pc derivative **3** after being exposed to PA showed significant changes compared to pristine phthalocyanine (Fig. 2b). The IR absorption band at 1588 cm^{-1} shifts to a higher frequency at 1633 cm^{-1} upon complexation with PA, indicating intermolecular π-π interaction and maintenance of the co-facial stacked geometry with PA.[14] Meanwhile, in the Raman spectrum of **3**, transitions were observed at 1450 and 2174 cm^{-1}, as shown in Fig. 2b (lower). In the presence of PA, these skeletal modes were still observable, although they shifted to lower values of 1442 and 2168 cm^{-1}. In addition, a new band was observed at 1372 cm^{-1}. Above observation indicates the formation of a charge-transfer (CT) complex between donor **3** and the acceptor PA. For

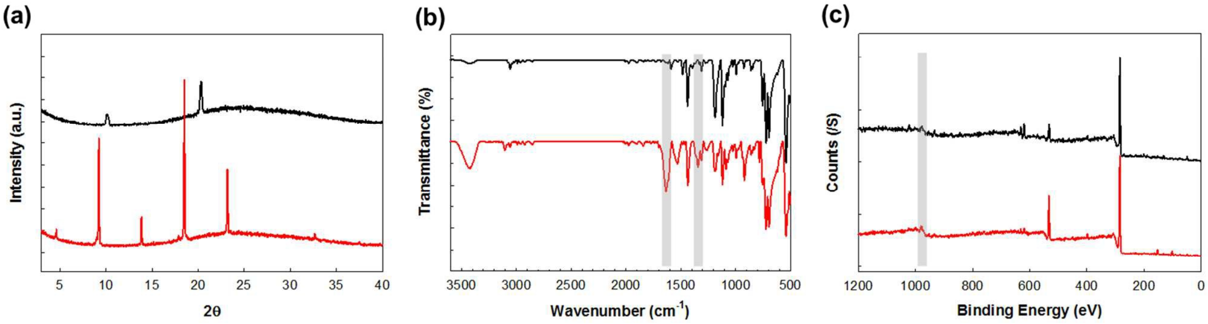
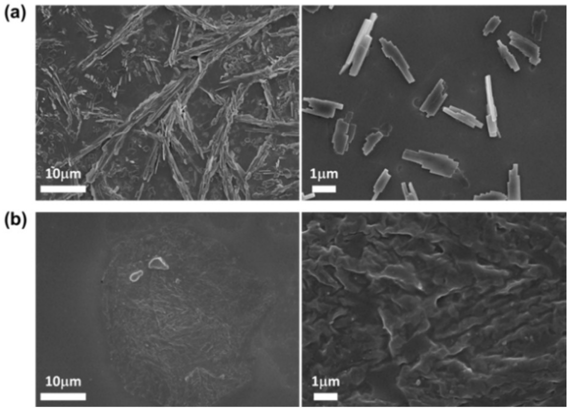


Fig. 2. (a) Wide-angle XRD patterns of **3** in the absence (black) and presence (red) of picric acid. (b) FT-IR spectra of **3** in the absence (black) and presence (red) of picric acid. (c) The XPS spectra of the corresponding samples are also shown.

more proof of interaction with PA, we recorded the XPS spectra of Pc derivative **3** in the presence of PA. A strong absorption peak around 1026 eV was observed, which was attributed to the typical signals for Zn^{2+} $2p_{3/2}$ (Fig. 2c). In the presence of PA, a slight chemical shift in the signal to a higher binding energy level was observed, indicating that PA interacts with **3**. It is also interesting to note, as evidenced in scanning electron microscopy (SEM) images, that such microscopic interactions were morphologically reflected by macroscopically aggregated structures. The SEM images of Pc-triad **3** showed the presence of fibers which were entangled with one another, resulting in an extended fibrillar network structure which is indicative of the tendency of the molecule to self-assemble into 1D fibers (Fig. 3a). It was clearly observed that the addition of PA leads to the formation of an irregular flake-like structure from the extended fibrillar network structure, providing evidence of interactions (Fig. 3b). In addition, the large surface-to-volume ratio of the one-dimensional extended fibrillar network structure leads to good contact with the PA, demonstrating good sensitivity.[15] The highly efficient fluorescence quenching of Pc-triad **3** by PA can be attributed to π-π interaction between the π-electron rich moieties in **3** and the quencher, PA. In principle, the quenching process is considered to be a photo-induced electron transfer (PET), in which the photo-induced electron on the LUMO of electron donor **3** transfers to its neighbouring electron acceptor, PA. The electron on the LUMO of an acceptor should then recombine with the donor's HOMO electron *via* a nonradiative process.



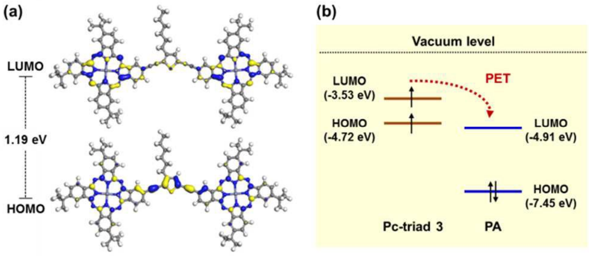


Fig. 3. SEM images of a thin film of **3** prepared (a) without and (b) with equimolar picric acid in a THF:water (6:4) mixture.

Fig. 4 (a) HOMO, and LUMO of Pc-triad **3** as calculated *via* density functional theory (DFT) calculations. (b) Proposed mechanism of the photo-induced electron transfer (PET) from Pc-triad **3** to the quencher (PA).

To investigate the characteristic energy trends based on the molecular orbitals of **3**, density functional theory (DFT) calculations were carried out with the general gradient approximation (GGA)-PBE functional [16] and DNP basis set using DMol3 module.[17] The HOMO of **3** is delocalized over the entire molecule but with a high concentration on central thiophene unit, whereas the LUMO electron is highly located on the Pc rings (Fig. 4a). It was clearly observed that a large π-electron overlap between the HOMO and LUMO of **3** was achieved by the introduction of a planar structure with two adjacent ethynylene-linked Pc rings and that its bandgap could therefore be lowered to 1.19 eV. It was also observed that the LUMO energies of **3** (-3.53 eV) and PA (-4.91 eV) are close, which supports the excited state electron-transfer from the LUMO of **3** to the lower energy LUMO of PA. The electron density distribution of LUMO corroborates the proposed π-π stacking interactions with PA, facilitating the electron transfer from the excited state of **3** to PA. A molecular orbital diagram of such a mechanism is schematically shown in Fig. 4b.

In summary, we demonstrate that the newly synthesized phthalocyanine-thiophene-phthalocyanine triad **3** (Pc-triad **3**) can function as a highly selective chemosensor against picric acid (PA). Pc-triad **3** showed efficient and selective fluorescence quenching towards PA, during which **3** exhibited a significant morphological change to an irregular flake-like structure from an extended fibrillar network structure. Various characterization techniques were successfully employed to analyze the intermolecular interaction of **3** with PA, revealing that PA molecules interacted with **3** *via* intermolecular π-π interaction and that the PET complex arose from the electron-rich pendant

Pc rings of **3** to the PA reagents, leading to the efficient fluorescence quenching of **3**.

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