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Fluorescent Tris-Imidazolium Sensors for Picric Acid Explosive

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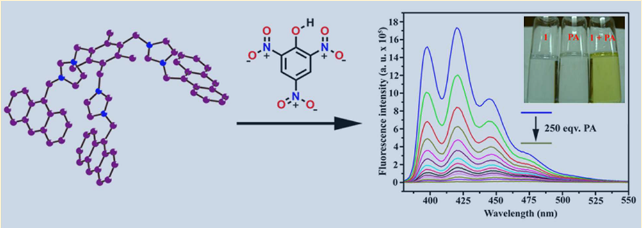
S Supporting Information

ABSTRACT: Two new anthracene-functionalized fluorescent tris-imidazolium salts have been synthesized, characterized, and proven to be selective sensors for picric acid, which is a common constituent of many powerful explosives. Theoretical studies revealed an unusual ground-state electron transfer from picrate anion to the sensor molecules.



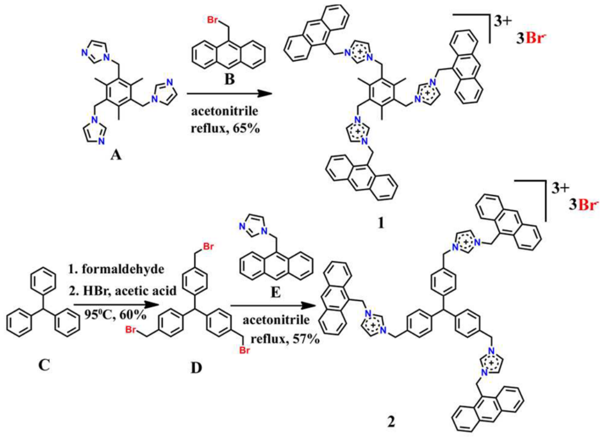
Picric acid (PA) is a strong organic acid,[1] and like many polynitrated aromatic compounds, it is a powerful explosive. Its explosive nature is even stronger than TNT, and it was widely used as an explosive until World War I.[2−5] Moreover, PA has importance in dye industries, pharmaceuticals, and chemical laboratories.[6,7] Instead of such importance, PA possesses acute health effects: it is a strong irritant to skin/eye and can cause potential damage to organs involved in the respiratory system.[8−10] It is to be noted that because of high solubility of PA in water, it can easily contaminate soil and groundwater when exposed. Hence, development of efficient sensors to detect PA at very low concentrations in order to prevent terrorist threats as well as environmental pollution is a very appealing field of research.[11]

Various methods have been employed for the detection of nitroaromatic explosives.[12−15] Among these, fluorescence sensing is widely employed because of its high sensitivity, quick response, easy sample preparation, etc.[16−18] Even though several π-electron-rich fluorescent organic polymers[19−22] and metal−organic architectures[23] have been employed to detect the presence of electron-deficient nitro-aromatics, development of suitable soluble and efficient organic chemosensors with high selectivity for PA is still a very challenging task.[24−29]

Imidazolium salts have been extensively studied as ionic liquids and N-heterocyclic carbene (NHC) precursors.[30−33] Recently, they have been tested as sensors for anions and biomolecules.[34,35] To the best of our knowledge, they have not yet been explored as sensors toward the detection of electron-deficient nitro-aromatics like picric acid. Herein, we report the syntheses and characterization of two tris-imidazolium salt based sensors **1** and **2** (Scheme 1), which have been proven to be potential candidates for picric acid sensing with high sensitivity and selectivity. The theoretical study revealed an unusual ground-state electron-transfer phenomenon from picrate anions to the positively charged sensors molecules.

Treatment of tris(*N*-imidazolylmethyl)mesitylene (**A**) with 9-bromomethylanthracene (**B**) in acetonitrile under refluxing conditions resulted in the formation of the sensor **1** (Scheme 1) with 65% yield. Tris(*p*-bromomethylphenyl)methane (**D**) was synthesized from triphenylmethane (**C**) following the standard bromomethylation reaction (Scheme 1).[36] Sensor **2** was synthesized similar to a procedure adopted for **1** upon treatment of **D** with 9-(*N*-imidazolylmethyl)anthracene (**E**, Scheme 1) with 57% yield.

Scheme 1. Schematic Presentation of the Synthesis of Sensors 1 and 2



Sensors **1** and **2** were purified by washing with acetonitrile several times followed by drying under vacuum and were fully characterized by NMR, solution-state ESI-MS, and elemental analyses. X-ray diffraction quality single crystals of **1** were obtained by slow evaporation of a solution of **1** in a MeOH−H_2O mixture. X-ray diffraction analysis revealed that **1** crystallized in the monoclinic crystal system with a *C*2/*c* space group. The crystallographic parameters of **1** are provided in Table S1 (see the Supporting Information). Among several possibilities, sensor **1** adopts *cis*,*cis*,*cis*-conformation and exhibits a bowl-shaped structure in the solid state (Figure 1). Several attempts to crystallize sensor **2** failed, but the DFT-optimized

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structure indicates a similar *cis,cis,cis*- conformational arrangement in the gas phase.

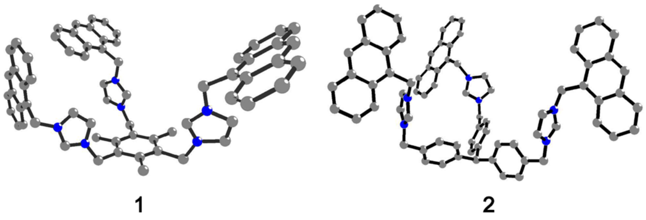

Figure 1. X-ray crystal structure of **1** (left) and energy-optimized structure of **2** (right). H atoms and Br^- ions are omitted for clarity. Color codes: C = gray and N = blue.

Both **1** and **2** exhibited almost identical spectral natures (UV−vis and fluorescence). The UV−vis absorption spectra in DMSO displayed absorption bands characteristic of anthracene[37] with absorption maxima (λ_{max}) at 352, 371, and 391 nm, while their emission spectra exhibited strong bands with emission maxima (λ_{max}) at 399, 422, and 446 nm upon excitation at 371 nm (Figure 2).

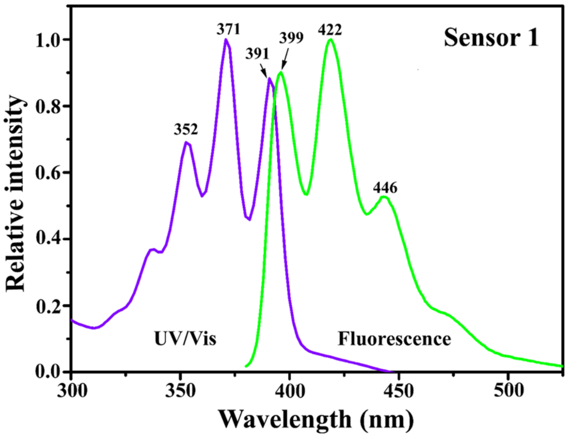

Figure 2. Absorption (violet) and emission (green) spectra of **1** in DMSO.

To judge the sensing ability of **1** and **2** toward electron-deficient nitro-aromatics, several analytes were used in $CHCl_3$ for fluorescence titration experiments. The fluorescence titration for sensor **1** and **2** with PA revealed that fluorescence emission intensity rapidly died down upon addition of increasing amounts of PA solution (Figure 3). The appearance of intense yellow color upon addition of colorless DMSO solution of sensor **1** to a pale yellow solution of PA in chloroform indicated the formation of [**1**⊃PA] complex (Figure 3). A similar observation was also noticed in the progress of the formation of [**2**⊃PA] (Figure S16, Supporting Information). The selectivity of the sensors was investigated by using several aromatic/nonaromatic compounds as analytes upon addition of 200 μL of 1 × 10^{-3} M analytes (100 equiv) solution in chloroform into 2 mL of 1 × 10^{-6} M solution of sensor (**1** or **2**) in DMSO. Interestingly, the quenching efficiencies of sensor **1** and **2** toward PA were found to be 92% and 91%, respectively, indicates their effectiveness to detect PA over other aromatic compounds (Figure 4).

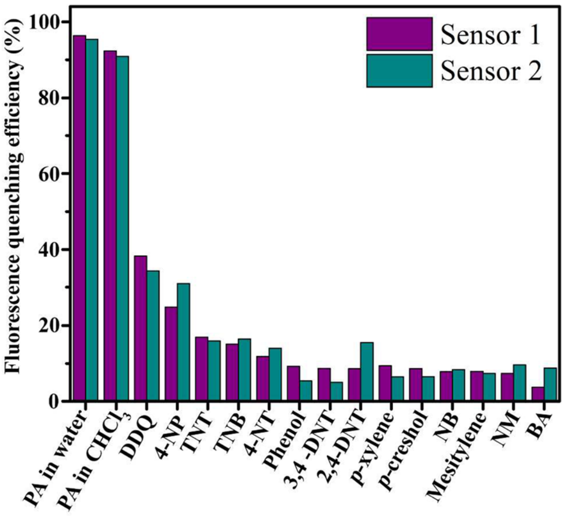

Figure 4. Fluorescence quenching efficiencies of sensors **1** and **2** toward different analytes. PA = picric acid; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; 4-NP = 4-nitrophenol; TNT = trinitrotoluene; TNB = trinitrobenzene; 4-NT = 4-nitrotoluene; 3,4-DNT = 3,4-dinitrotoluene; 2,4-DNT = 2,4-dinitrotoluene; NB = nitrobenzene; NM = nitromethane; BA = benzoic acid.

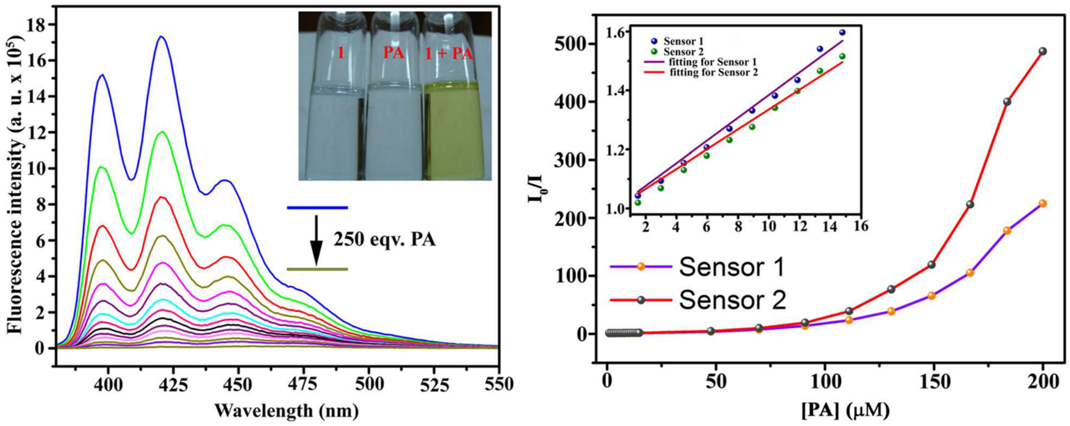

Figure 3. (Left) Fluorescence intensity vs analyte concentration plot for sensor **1** titrated upon gradual addition of PA. Inset: visual color change due to the formation [**1**⊃PA] complex. (Right) Stern−Volmer plots for sensors **1** and **2** using PA as quencher. Inset: Stern−Volmer plots at lower concentration region of PA.

This fact is again supported by high Stern−Volmer constants K_{SV} = 3.8 × 10^4 M^{-1} and 3.3 × 10^4 M^{-1} for sensors **1** and **2**, respectively. The Stern−Volmer plots showed two distinct regions: linear variation at a lower concentration of PA is mainly due to static quenching, whereas a steep curve at higher concentration of PA is presumably due to dynamic quenching. The static quenching can be attributed due to the ground-state charge-transfer complex formation, which is confirmed by UV−vis (Figure S17, Supporting Information) and NMR experiments as well as single-crystal X-ray diffraction. However, the dynamic quenching mechanism is confirmed by the fluorescence lifetime measurement (Figure S18, Supporting Information).

Significant UV−vis spectral changes with the appearance of a new band at 430 nm in comparison to the UV−vis spectra of free sensors and PA indicated their complex formation [**1**/**2**⊃PA] (Figure S17, Supporting Information). The [**1**⊃PA] and [**2**⊃PA] were isolated as yellow precipitates from a methanolic solution of **1**/**2** and PA.

The ^{1}H NMR spectral analyses of [**1**⊃PA] and [**2**⊃PA] showed the presence of PA with significant shifts of the sensors peak positions (Figure 5) and also confirmed the formation of complexes between the sensors (**1** or **2**) with PA in 1:2 molar ratios (Figure S12, Supporting Information). Job's plot analysis experiment for the determination of stoichiometry was inconclusive because of the overlapping absorption wavelength regions for sensors and PA (for PA, λ_{max}= 356 nm in water, 336 nm in CH_2Cl_2 and 378 nm in DMSO).

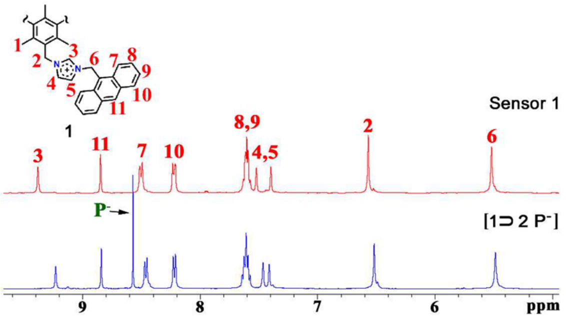

Figure 5. ^{1}H NMR spectra of sensor **1** (red) and its PA complex (blue) in DMSO-d_6.

Finally, X-ray diffraction study on single crystals of [**1**⊃PA] as obtained from slow vapor diffusion of ethyl acetate into acetonitrile solution of [**1**⊃PA] unambiguously confirmed the formation of the [**1**⊃2PA] complex. Although the quality of the diffraction data of [**1**⊃2PA] was poor, the present data set clearly indicated the presence of two picrate (**P**$^-$) ions per molecule upon replacing two bromide counteranions from **1** and their locations (Figure S3, Supporting Information). The [**1**⊃2P$^-$] crystallized in monoclinic crystal system with *Pc* space group. The solid-state packing diagram revealed that picrate moieties formed columnar arrangement intervened between anthracene moieties of the sensor molecules via mainly π−π stacking interactions (Figure S3, Supporting Information).

To our surprise, the ground-state charge transfer occurs from picrate anions to the positively charged sensor molecules in the gas phase as evident from the DFT calculations. The DFT studies revealed that the energy of the highest occupied molecular orbital (HOMO) of the free sensor **1** is −0.406 eV and the energy of the lowest occupied molecular orbital (LUMO) of **1** is −0.312 eV (Figure 6), while the energies of HOMO and LUMO of picrate anion are −0.125 eV and +0.005 eV, respectively. Hence, the ground-state electronic charge transfer takes place from the HOMO of picrate anion to the LUMO of sensor **1**.

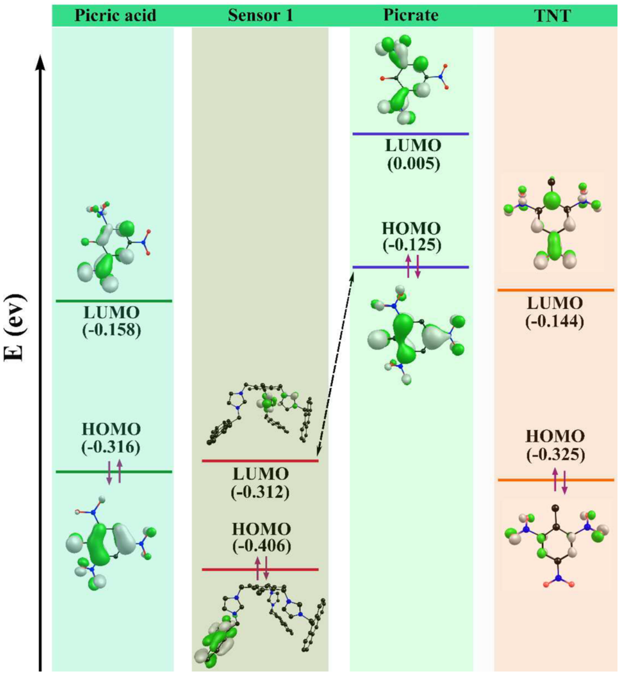

Figure 6. Pictorial representation of the charge transfer phenomenon in the ground state which occurs from the HOMO of picrate anion to the LUMO of sensor **1** and also compared with TNT.

The sensors **1** and **2** are highly sensitive and can detect PA down to 467 and 354 ppb, respectively (Supporting Information). To check the efficiency of the sensors in aqueous media, DMSO solutions of **1** and **2** were titrated with aqueous solution of PA. The similar large value of quenching efficiencies in aqueous media indicated the potential applicability of **1** and **2** for the detection of PA in groundwater (Supporting Information). Though PA and TNT have similar reduction potentials (RNO_2/RNO_2^- = −0.39 V for PA and −0.30 V for TNT),[38] considerably high quenching efficiencies observed for only PA (91% for **1** and 92% for **2**) in comparison to TNT (17% for **1** and 16% for **2**) (Figure 4) can be attributed to deprotonation of the strongly acidic phenolic −OH group followed by anion exchange with the sensor molecules. Moreover, the theoretical calculations also revealed the lower quenching efficiency of TNT because its HOMO (HOMO and LUMO energies are −0.325 and −0.144 eV, respectively) has lower energy than the LUMO of sensor (Figure 6).

In conclusion, we have reported two tris-imidazolium salts (**1** and **2**) that selectively sense PA at the ppb level in both organic and aqueous media. To the best of our knowledge, compounds **1** and **2** represent the first examples of imidazolium salts potential for the detection of trace amount of powerful explosive picric acid. The crystal structures of sensor **1** and its PA complex [**1**⊃2P$^-$] were successfully established by X-ray crystallography. In the complex [**1**⊃2P$^-$], picric acid exists as picrate ion upon deprotonation, which leads to quenching of fluorescence of **1**.

EXPERIMENTAL SECTION

The synthesis of tris(*N*-imidazolylmethyl)mesitylene (**A**) from trisbromomethylmesitylene was carried out by following the standard literature procedure.[39] 9-(Bromomethyl)anthracene (**B**) was synthesized in two steps involving reduction of 9-anthracenecarboxaldehyde to the corresponding alcohol followed by substitution of −OH group by bromine using reported methodologies.[40] 9-(*N*-Imidazolylmethyl)-anthracene (**E**) was also synthesized by a known literature procedure.[41]

Caution! The nitroaromatic compounds used in this study, specially TNT and picric acid, are very powerful explosives. They must be handled with care and also in very small quantities.

Synthesis of Tris(*p*-bromomethylphenyl)methane (D). Triphenylmethane (5 g, 20.46 mmol), paraformaldehyde (5 g), and 33% HBr in acetic acid (50 mL) were taken in a 250 mL round-bottom flask and heated at 120 °C with stirring for 24 h. The solution was then poured into 500 mL of ice-cold water to obtain a dark yellow solid which was collected by filtration and subsequently washed with plenty of water and dried in an oven at 60 °C overnight. The compound was purified by column chromatography by eluting with a 5% DCM/hexane mixture. Isolated yield = 6.3 g (59%). Mp = 101 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (d, 6H), 7.06 (d, 6H), 5.50 (s, 1H), 4.48 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.9, 136.5, 130.2, 129.6, 56.4, 33.7. Anal. Calcd (vacuum-dried sample) for $C_{22}H_{19}Br_3$: C, 50.51; H, 3.66. Found: C, 50.77; H, 3.38;

Synthesis of Sensor 1. Tris(*N*-imidazolylmethyl)mesitylene (**A**) (300 mg, 0.83 mmol) and 9-bromomethylanthracene (**B**) (676.7 mg, 2.5 mmol) were dissolved in 50 mL of acetonitrile, and the solution was refluxed for 72 h. The light brown solid formed was isolated by filtration followed by washing with acetonitrile. Isolated yield = 635 mg (65%). Mp = 228 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.38 (s, 3H), 8.85 (s, 3H), 8.50 (d, 6H), 8.21 (d, 6H), 7.60 (m, 12H), 7.52 (s, 3H), 7.40 (s, 3H), 6.57 (s, 6H), 5.52 (s, 6H), 2.21 (s, 9H). ^{13}C NMR (methanol-d_4, 100 MHz): δ 142.3, 136.1, 132.0, 131.4, 130.8, 129.8, 129.7, 128.1, 125.6, 123.0, 122.9, 122.7, 122.3, 45.8, 15.9. MS (ESI) = m/z 1093.15 [**1** − Br$^-$]$^+$, 506.11 [**1** − 2Br$^-$]$^{2+}$. Anal. Calcd (vacuum-dried sample) for $C_{66}H_{57}Br_3N_6$: C, 67.53; H, 4.89; N, 7.16. Found: C, 67.79; H, 4.70; N, 7.38.

Synthesis of Sensor 2. Sensor **2** was synthesized by the same procedure as adopted for **1** by refluxing a solution of tris(*p*-bromomethylphenyl)methane (**D**) (300 mg, 0.58 mmol) and 9-(*N*-imidazolylmethyl)anthracene (**E**) (666.6 mg, 2.58 mmol) in 50 mL of acetonitrile for 72 h. The product was isolated as deep brown solid which was hygroscopic. Isolated yield = 424 mg (57%). Mp = 222 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.13 (s, 3H), 8.85 (s, 3H), 8.44 (d, 6H), 8.22 (d, 6H), 7.60 (m, 18H), 7.24 (d, 6H), 7.07 (d, 6H), 6.49 (s, 6H), 5.60 (s, 1H), 5.29 (s, 6H). ^{13}C NMR (methanol-d_4, 100 MHz): δ 144.7, 136.1, 132.7, 132.0, 131.3, 130.9, 130.2, 129.8, 128.7, 128.2, 125.6, 123.0, 122.9, 122.7, 122.4, 55.9, 52.7, 45.8. MS (ESI): m/z = 1217.20 [**2** − Br$^-$]$^+$, 568.38 [**2** − 2Br$^-$]$^{2+}$, 352.27 [**2** − 3Br$^-$]$^{3+}$. Anal. Calcd (vacuum-dried sample) for $C_{76}H_{61}Br_3N_6$: C, 70.32; H, 4.74; N, 6.47. Found: C, 70.03: H, 4.98; N, 6.58.

Synthesis of [1⊃2P$^-$] Complex. Twenty milligrams (0.017 mmol) of **1** was dissolved in methanol and added to a methanolic solution of PA (23.4 mg, 0.102 mmol) to obtain heavy yellow precipitate. The solution was stirred for 3 h at room temperature. Then it was centrifuged and washed with methanol. Isolated yield = 23.7 mg (95%). Mp =166 °C. ^{1}H NMR (acetone-d_6, 400 MHz): δ 10.70 (s, 3H), 8.83 (s, 3H), 8.71 (d, 6H), 8.62 (s, 4H), 8.21 (d, 6H), 7.99 (s, 3H), 7.55 (m, 12H), 7.24 (s, 3H), 7.00 (s, 6H), 5.87 (s, 6H), 2.59 (s, 9H). ^{13}C NMR (acetonitrile-d_3, 100 MHz): δ 161.9, 142.6, 136.3, 131.9, 131.4, 130.9, 130.0, 128.3, 126.0, 125.9, 125.5, 123.5, 123.0, 122.4, 48.8, 46.0, 16.4. Anal. Calcd (vacuum-dried sample) for $C_{78}H_{61}BrN_{12}O_{14}$: C, 63.72; H, 4.18; N, 11.43. Found: C, 63.77; H, 4.28; N, 11.59.

Synthesis of [2⊃2P$^-$] Complex. [2⊃2P$^-$] was prepared in similar way by treating 20 mg (0.015 mmol) of **2** with 21.1 mg (0.094 mmol) of PA in methanol. Isolated yield = 22.6 mg (92%). Mp = 145 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.10 (s), 8.83 (s), 8.56 (s), 8.41 (d), 8.20 (d), 7.64 (m), 7.22 (d), 7.08 (d), 6.48 (s), 5.58 (s), 5.28 (s). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 161.2, 144.0, 142.1, 136.1, 133.3, 131.4, 130.9, 130.5, 129.7, 128.6, 128.0, 125.9, 125.5, 124.5, 123.5, 123.3, 122.9, 68.8, 51.8, 45.4. Anal. Calcd (vacuum-dried sample) for $C_{88}H_{65}BrN_{12}O_{14}$: C, 66.29; H, 4.11; N, 10.54. Found: C, 65.93; H, 4.32; N, 10.23.

ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR of all new compounds, ESI-MS, UV−vis, and fluorescence spectra, X-ray crystal data, thermal ellipsoid plots of **1** and [**1**⊃2P$^-$], and tables for optimized coordinates. This material is available free of charge via the Internet at http://pubs.acs.org. .

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Perez, G. V.; Perez, A. L. *J. Chem. Educ.* **2000**, *77*, 910.

(2) Akhavan, J. *Chemistry of Explosives*, 2nd ed.; Royal Society of Chemistry: London, 2004.

(3) Cooper, P. *Explosive Engeneering*; Wiley-VCH: New York, 1996; p 33.

(4) United States Patent 3515604.

(5) Muthurajan, H.; Sivabalan, R.; Talawar, M. B.; Asthana, S. N. *J. Hazard. Mater.* **2004**, *A112*, 17.

(6) Meredith, D. T.; Lee, C. O. *J. Am. Pharm. Assoc.* **1939**, *28*, 369.

(7) Volwiler, E. H. *Ind. Eng. Chem.* **1926**, *18*, 1336.

(8) Safety Data Sheet for Picric Acid, Resource of National Institute of Health.

(9) Ashbrook, P. C.; Houts, T. A. *ACS Div. Chem. Health Safety* **2003**, *10*, 27.

(10) Cameron, M. *Picric Acid Hazards*; American Industrial Hygiene Association: Fairfax, VA, 1995.

(11) Nipper, M.; Qian, Y.; Carr, R. S.; Mkiller, K. *Chemosphere* **2004**, *56*, 519.

(12) Moore, D. S. *Rev. Sci. Instrum.* **2004**, *75*, 2499.

(13) Zimmermann, Y.; Broekaert, J. A. C. *Anal. Bioanal. Chem.* **2005**, *383*, 998.

(14) Steinfeld, J. I.; Wormhoudt, J. *Annu. Rev. Phys. Chem.* **1998**, *49*, 203.

(15) Soltzberg, L. J.; Hagar, A.; Kridaratikorn, S.; Mattson, A.; Newman, R. *J. Am. Soc. Mass Spectrom.* **2007**, *18*, 2001.

(16) Germain, M. E.; Knapp, M. J. *Chem. Soc. Rev.* **2009**, *38*, 2543.

(17) Shanmugaraju, S.; Joshi, S. A.; Mukherjee, P. S. *J. Mater. Chem.* **2011**, *21*, 9130.

(18) Lee, Y. H.; Liu, H.; Lee, J. Y.; Kim, S. H.; Kim, S. K.; Sessler, J. L.; Kim, Y.; Kim, J. S. *Chem.—Eur. J.* **2010**, *16*, 5895.

(19) Toal, S. J.; Trogler, W. C. *J. Mater. Chem.* **2006**, *16*, 2871.

(20) Sohn, H.; Calhoun, R. M.; Sailor, M. J.; Trogler, W. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2104.

(21) Thomas, S. W., III; Joy, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339.

(22) Kartha, K. K.; Babu, S. S.; Srinivasan, S.; Ajayghosh, A. *J. Am. Chem. Soc.* **2012**, *134*, 4834.

(23) (a) Vajpayee, V.; Kim, H.; Mishra, A.; Mukherjee, P. S.; Stang, P. J.; Lee, M.; Kim, H. K.; Chi, K. W. *Dalton Trans.* **2011**, *40*, 3112.

(b) Pramanik, S.; Zheng, C.; Zhang, X.; Emge, T. J.; Li, J. *J. Am. Chem. Soc.* **2011**, *133*, 4153.

(24) Zeng, H. H.; Wang, K. M.; Yu, R. Q. *Anal. Chim. Acta* **1994**, *298*, 271.

(25) Peng, Y.; Zhang, A. J.; Dong, M.; Wang, Y. W. *Chem. Commun.* **2011**, *47*, 4505.

(26) He, G.; Peng, H.; Liu, T.; Yang, M.; Zhangand, Y.; Fang, Y. *J. Mater. Chem.* **2009**, *19*, 7347.

(27) Gole, B.; Shanmugaraju, S.; Bar, A. K.; Mukherjee, P. S. *Chem. Commun.* **2011**, *47*, 10046.

(28) Kim, D. S.; Lynch, M.; Nielson, K. A.; Johnsen, C.; Jeppesen, J. O.; Sessler, J. L. *Anal. Bioanal. Chem.* **2009**, *395*, 393.

(29) Shanmugaraju, S.; Joshi, S. A.; Mukherjee, P. S. *Inorg. Chem.* **2011**, *50*, 11736.

(30) Hindi, K. M.; Panzner, M. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. *Chem. Rev.* **2009**, *109*, 3859.

(31) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 362.

(32) Ahrens, S.; Peritz, A.; Strassner, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 7908.

(33) Dupont, J.; Spencer, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5296.

(34) (a) Coll, C.; Manez, R. M.; Marcos, M. D.; Sansenon, F.; Soto, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 1675. (b) Chen, X.; Kang, S.; Kim, M. J.; Kim, J.; Kim, Y. S.; Kim, H.; Chi, B.; Kim, S.-J.; Lee, J. Y.; Yoon, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 1422. (c) Xu, Z.; Kim, S. K.; Yoon, J. *Chem. Soc. Rev.* **2010**, *39*, 1457.

(35) (a) Jung, J. Y.; Jun, E. J.; Kwon, Y. U.; Yoon, J. *Chem. Commun.* **2012**, *48*, 7928. (b) Guo, Z.; Song, N. R.; Moon, J. H.; Kim, M.; Jun, E. J.; Choi, J.; Lee, J. Y.; Bielawski, C. W.; Sessler, J. L.; Yoon, J. *J. Am. Chem. Soc.* **2012**, *134*, 17846.

(36) Made, A. W. V.; Made, R. H. V. *J. Org. Chem.* **1993**, *58*, 1262.

(37) Sidman, J. W. *J. Chem. Phys.* **1956**, *25*, 114.

(38) Uchimiya, M.; Gorb, L.; Isayev, O.; Qasim, M. M.; Leszczynski, J. *Environ. Pollut.* **2010**, *158*, 3048.

(39) Yuan, Y.; Jiang, Z. L.; Yan, J. M.; Gao, G.; Chan, A. S. C.; Xie, R. G. *Synth. Commun.* **2000**, *30*, 4555.

(40) Ostaszewski, R.; Wilczynska, E.; Wolszczak, M. *Bioorg. Med. Chem. Lett.* **1998**, *8*, 2995.

(41) Neelakandan, P. P.; Ramaiah, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 8407.