ChemComm

RSCPublishing

COMMUNICATION

View Article Online
View Journal

Tunable star-shaped triphenylamine fluorophores for fluorescence quenching detection and identification of nitro-aromatic explosives†

Cite this: DOI: 10.1039/c2cc34008a

Received 5th June 2012,
Accepted 4th December 2012

DOI: 10.1039/c2cc34008a

www.rsc.org/chemcomm

Nakorn Niamnont,[ab] Nattaporn Kimpitak,[a] Kanet Wongravee,[a] Paitoon Rashatasakhon,[a] Kim K. Baldridge,[c] Jay S. Siegel*[c] and Mongkol Sukwattanasinitt*[a]

Triphenylamine-based fluorophores containing pyrene or corannulene show variable fluorescence quenching sensitivity toward nitro explosives. The most sensitive fluorophore is capable of detecting TNT on the ng cm^{-2} scale; the array is useful for identifying nitro aromatics.

Detection of trace explosives, such as 2,4,6-trinitrotoluene (TNT), is of great social concern.[1] Fluorescence quenching provides a mechanism suitable for a real-time TNT sensor.[2] The demand for detectors of higher sensitivity and accuracy requires agents for selective and sensitive TNT sensing. To address these issues, four triskelion-shaped fluorophores were designed containing an electron donating triphenylamine core coupled, by either ethynylene or triazole linkers, to a fluorescent polynuclear aromatic hydrocarbon (PAH) unit (Fig. 1). Specifically, compounds bearing the bowl-shaped corannulene ring (TEC; TAC) were compared with analogs bearing a planar polyaromatic pyrene ring (TEP; TAP). Their sensing properties for the detection of TNT and analogous compounds are reported herein.

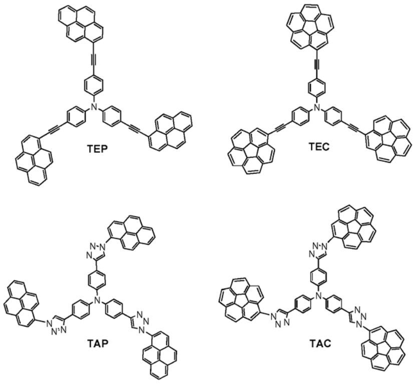

Fig. 1 Structures of fluorophores.

Fluorescence quenching efficiency is normally rated by the Stern–Volmer constant (K_{sv}).[3] Such quenching, between an electron rich fluorophore and electron poor TNT, is associated with an intermolecular photoinduced electron transfer.[4] This electron transfer efficiency relies heavily on the π–π interaction between TNT and the fluorophore; in addition, the LUMO energy level of the fluorophore has to be higher than the HOMO energy level of TNT. Indeed, pyrene derivatives, with large delocalized π systems and well-matched orbital energy levels, show good selectivity and sensitivity for the detection of TNT.[5] Amplification of fluorescence quenching has been achieved by incorporation of multiple fluorescent units, which interact through efficient energy and electron transfer.[5b,6] Cooperative π–π interactions with TNT can also enhance sensitivity.[7]

The ethynylene linked triskelion branched fluorophores TEP and TEC were synthesized from 4,4′,4″-triiodotriphenylamine[8] *via* Sonogashira cross coupling reaction with ethynylpyrene[9] and ethynylcorannulene.[10] The triazole linked TAP and TAC were obtained from the click reaction between 4,4′,4″-triethynyltriphenylamine[11], 1-azidopyrene[12] and 1-azidocorannulene.[13] The detailed synthetic procedures and spectroscopic data for all fluorophores are available in the ESI.†

The UV-Vis absorption spectrum of each fluorophore in chloroform showed a more structured absorption band at higher energy (λ_{max} < 300 nm) corresponding to a local π–π* local transition and a broad absorption (λ_{max} > 300 nm) associated with the π–π* electronic transition of the whole conjugated system (Fig. S5.1, ESI†). The latter λ_{max} is thus related to the π-electron delocalization in the HOMO level. TEP and TEC possess significantly longer λ_{max} (415 and 421 nm) than those of TAP and TAC (346 and 329 nm), which suggests greater electron delocalization in TEC and TEP compared to TAP and TAC. The λ_{em} of TEP and TEC (484 and 494 nm) appeared at considerably higher energy than those of TAP and TAC (506 and 537 nm) and the large Stokes shifts (~200 nm)

---

[a] *Organic Synthesis Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University and Nanotec-CU Center of Excellence on Food and Agriculture, Bangkok 10330, Thailand. E-mail: smongkol@chula.ac.th; Fax: +66 2 2187598; Tel: +66 2 2187620*

[b] *Department of Chemistry, Faculty of Science, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand*

[c] *Organic Chemistry Institute, University of Zurich, Winterthurerstrasse 190, Zurich, 8057, Switzerland. E-mail: jss@oci.uzh.ch; Fax: +41 44 635 6888; Tel: +41 44 635 4201*

† Electronic supplementary information (ESI) available: Synthesis and characterization data. See DOI: 10.1039/c2cc34008a

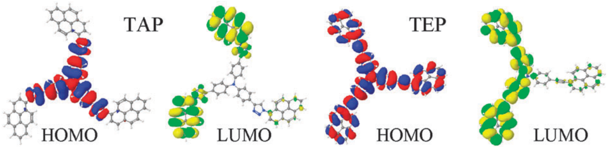

Fig. 2 HOMO–LUMO of TAP and TEP.

for TAC and TAP suggest a nuclear or electronic structure in their excited states (*i.e.* a conformational change like flattening or more likely an electronic redistribution like charge transfer).[14] The lower fluorescence quantum yields (Φ_F) of TAP and TAC (4.6% and 9.6%) compared to TEP and TEC (24% and 19%) further support this hypothesis.

B97D/Def2-TZVPP calculations[15] on all four fluorophores depict the greater delocalization of the MOs in TEP and TEC in comparison with TAP and TAC as well as the shift from the core to the periphery for the HOMO *vs.* the LUMO of TAP and TAC (Fig. 2). Calculations further confirmed that the TNT LUMO level (−4.27 eV) is located between the HOMO and LUMO levels of TAP and TAC. Indeed, predicted IP values (ΔSCF) for TEP, TEC, TAP, TAC are 5.42, 5.65, 5.62, 5.75 eV, respectively, which support their electron donor character.

The emission spectra of TAP in the presence of various concentrations of TNT (Fig. 3, left) demonstrated efficient fluorescence quenching. The quenching efficiency by TNT of each fluorophore was determined from the Stern–Volmer plot[4] in comparison with the underivatized corannulene (Co) and pyrene (Py) (Fig. 3, right). The plots clearly showed that the fluorescence quenching of TAP and TAC was much more sensitive than their parent fluorophores, pyrene and corannulene. Despite having the same number of fluorogenic units, TEP and TEC displayed significantly lower quenching efficiencies ($K_{sv} = 8.4 \times 10^2$ and $7.2 \times 10^2\ \mathrm{M}^{-1}$) than those of TAP and TAC ($K_{sv} = 1.7 \times 10^4$ and $6.4 \times 10^3\ \mathrm{M}^{-1}$). In fact TEP and TEC hardly showed any signal quenching amplification. The results suggested that the triazole bridge must play an important role in enhancing quenching.

^{1}H NMR spectroscopy of TAP and TNT showed that the proton signals of the pyrene and triazole units were clearly shifted upon the addition of 100 equiv. of TNT (Fig. 4). Notably, the downfield shift of the triazole proton (H_j) singlet signal suggests an interaction between H_j and the nitro group. The upfield shifts of pyrene signals (a–i) are consistent with the π–π interaction between the pyrene and nitroaromatic ring.[5a]

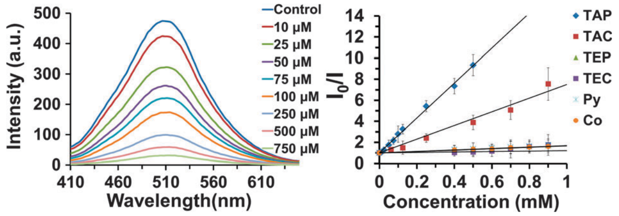

Fig. 3 (left) Emission spectra of TAP (0.1 μM in $CHCl_3$; λ_{ex} = 345 nm) in the presence of TNT at various concentrations. (right) Stern–Volmer plots for quenching of the fluorophores with TNT at 25 °C.

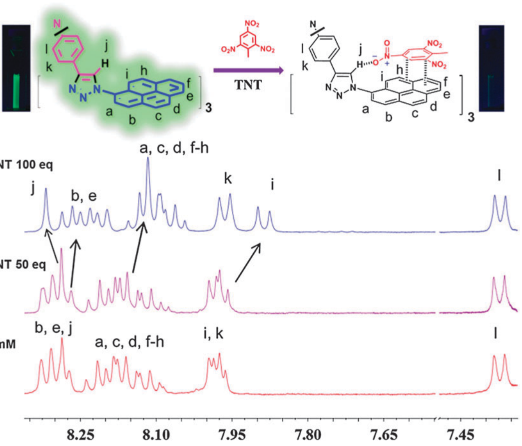

Fig. 4 ^{1}H NMR of TAP (0.1 mM in $CDCl_3$) in the absence and presence of TNT. The top diagram is the proposed TAP–TNT interaction geometry.

The supramolecular complexation, and thus the fluorescence quenching, between our analytes and TNT likely occurs through a dynamic process. The ^{1}H NMR shows a commensurate shift with increasing addition of TNT and no signals for the fluorophore independent of the fluorophore–TNT complex are evident. The K_{sv} values obtained from the quenching experiments at 5 °C to 45 °C were $1.4 \times 10^4\ \mathrm{M}^{-1}$ and $2.0 \times 10^4\ \mathrm{M}^{-1}$, respectively (Fig. S7.2, ESI†). The increase in K_{sv} values with temperature supports the dynamic quenching mechanism.[4d]

Underivatized corannulene and TEC ($K_{sv} = 6.7 \times 10^2$ and $7.2 \times 10^2\ \mathrm{M}^{-1}$) exhibited slightly lower K_{sv} values than those for the corresponding pyrene systems ($K_{sv} = 7.8 \times 10^2$ and $8.4 \times 10^2\ \mathrm{M}^{-1}$). More significantly, TAC gave three times lower quenching efficiency than TAP ($K_{sv} = 6.4 \times 10^3$ *vs.* $1.7 \times 10^4\ \mathrm{M}^{-1}$). We attribute the lower sensitivity of the corannulene to its bowl shape geometry, which probably does not well accommodate the π–π interaction with TNT, required for an efficient photoinduced electron transfer quenching process.

To evaluate the selectivity of the fluorophores, nine aromatic compounds (phenol, benzoic acid, benzophenone, nitrobenzene, 3-nitrophenol, 2,4-dinitrophenol (DNP), nitrotoluene, 2,4-dinitrotoluene and TNT) were tested as quenchers. The K_{sv} value of each quencher–fluorophore pair was determined. Overall, TAP showed the highest sensitivity toward TNT ($K_{sv} = 1.7 \times 10^4\ \mathrm{M}^{-1}$) and a TNT : DNP selectivity ratio of 4.3 (Fig. S8.2, ESI†). TAC exhibited lower sensitivity ($6.4 \times 10^3\ \mathrm{M}^{-1}$) as well as selectivity (TNT : DNP ~ 1.6).

All the fluorophores generally exhibited greater fluorescence quenching with electron deficient nitroaromatic compounds than with other aromatic compounds; nonetheless, the variation in quenching profiles provided patterns useful for identification of the quencher. The change in fluorescence intensities of the four fluorophores ($\Delta I = I_0 - I$) in the absence (I_0) and presence (I) of each aromatic compound, at fixed absorbance ($A(\lambda_{max}) = 0.01$), was acquired. Using a non-supervised multivariate principal component analysis (PCA) method,[16] the total intensity changes (430–600 nm) were transformed into principal components (PCs). The PCA score plot in 2D space of PC1 and PC2 statistically demonstrated nine identifiable clusters of data, obtained from 4 fluorophores × 9 aromatic samples × 9 measurements, with a total variance of 86.7%. A cross validation by linear discriminant analysis (LDA),[17] a supervised method,[18] on the PC scores gave 96.3%

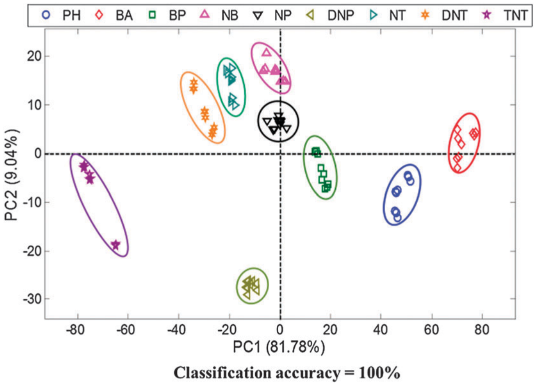

Fig. 5 PC score plot of Δ*I* of the fluorophores (*A* = 0.01 @ 500 nm).

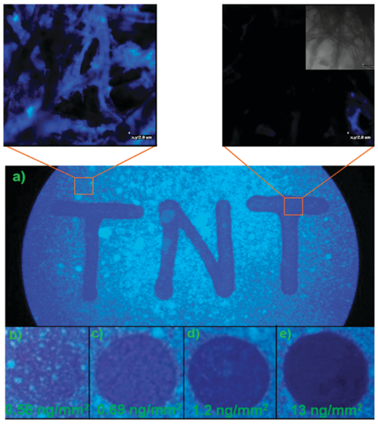

Fig. 6 (a) TNT stains on a filter paper sprayed with TAP (20 μM in $CHCl_3$–toluene (1/3 v/v)); fluorescence microscopy images of areas with (top right) and without (top left) TNT. (b–e) Varying amounts of TNT.

accuracy of classification of the nine aromatic samples. Cross validation, performed at each wavelength within the 480–530 nm range, revealed that correct classification was achieved from the data at individual wavelengths; results from Δ*I* at 500 nm give the total variance of the first two PCs as high as 90.8% with 100% classification accuracy (Fig. 5).

A PCA loading plot identified TAC and TAP as the most dominant fluorophore contributors to PC1 and PC2, respectively; however, the PCA score plot of these two fluorophores at 500 nm showed poor separation among data groups and the classification accuracy dropped to 95.06%. A classification accuracy of 100% was obtained only from the combination of all fluorophores; thus, all four fluorophores are needed to identify these nine electron deficient aromatic compounds uniquely.

Visual detection of trace explosives is very convenient for security screening. Spraying TAP solution on top of a filter paper tainted with trace TNT (50 μM in ethanol) clearly revealed a darker pattern under common black light illumination (Fig. 6). Under a fluorescence microscope, the TNT mark appeared dark providing high contrast with the blue luminescence of the untainted area; the technique readily allowed visual detection of TNT down to 0.58 ng mm^{-2}, which is about ten times lower than the lowest number previously reported.[19]

In conclusion, the triazole unit can be used to increase the TNT quenching sensitivity of triphenylamine based fluorophores containing multiple pyrenes to the level that visual detection of TNT on the ng mm^{-2} scale was possible. The series of triphenylamine based fluorophores containing multiple pyrene and corannulene was capable of identifying electron deficient aromatic compounds including TNT and DNT.

We would like to thank the Thailand Nanotechnology Center (NANOTEC), the IIAC Chulalongkorn University Centenary Academic Development Project, the National Research University Project of Thailand, Office of the Higher Education Commission (AM1006A), the 90th Anniversary Fund of CU and the Swiss National Foundation for financial support.

Notes and references

1 (*a*) A. W. Czarnik, *Nature*, 1998, **394**, 417; (*b*) K. J. Albert, N. S. Lewis, C. L. Schauer, G. A. Sotzing, S. E. Stitzel, T. P. Vaid and D. R. Walt, *Chem. Rev.*, 2000, **7**, 2595.
2 (*a*) A. Rose, Z. G. Zhu, C. F. Madigan, T. M. Swager and V. Bulovic, *Nature*, 2005, **434**, 876; (*b*) E. R. Goldman, I. L. Medintz, J. L. Whitley, A. Hayhurst, A. R. Clapp, H. T. Uyeda, J. R. Deschamps, M. E. Lassman and H. Mattoussi, *J. Am. Chem. Soc.*, 2005, **127**, 6744.
3 (*a*) J. S. Yang and T. M. Swager, *J. Am. Chem. Soc.*, 1998, **120**, 11864; (*b*) S. J. Toal, D. Magde and W. C. Trogler, *Chem. Commun.*, 2005, 5465; (*c*) G. V. Zyryanov, M. A. Palacios and P. J. Anzenbacher, *Org. Lett.*, 2008, **10**, 3681; (*d*) Y. Y. Long, H. B. Chen, Y. Yang, H. M. Wang, Y. F. Yang, N. Li, K. A. Li, J. Pei and F. Liu, *Macromolecules*, 2009, **42**, 6501; (*e*) W. Chen, N. B. Zuckerman, J. P. Konopelski and S. Chen, *Anal. Chem.*, 2010, **82**, 461; (*f*) H. Nie, Y. Zhao, M. Zhang, Y. Ma, M. Baumgarten and K. Mullen, *Chem. Commun.*, 2011, **47**, 1234.
4 (*a*) S. J. Toal and W. C. Trogler, *J. Mater. Chem.*, 2006, **16**, 2871; (*b*) S. W. Thomas, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339; (*c*) M. E. Germain and M. J. Knapp, *Chem. Soc. Rev.*, 2009, **38**, 2543; (*d*) J. R. Lakowicz, *Principles of fluorescence spectroscopy*, John Wiley & Sons, Inc., Kluwer, 3rd edn, 2006.
5 (*a*) 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; (*b*) H. Wang, L. Ding, S. Yin and Y. Fang, *Macromolecules*, 2011, **44**, 4759.
6 H. Cavaye, P. E. Shaw, X. Wang, P. L. Burn, S.-C. Lo and P. Meredith, *Macromolecules*, 2010, **43**, 10253.
7 (*a*) D. A. Olley, E. J. Wren, G. Vamvounis, M. J. Fernee, X. Wang, P. L. Burn, P. Meredith and P. E. Shaw, *Chem. Mater.*, 2011, **23**, 789; (*b*) G. Q. Tang, S. S. Y. Chen, P. E. Shaw, K. Hegedus, X. Wang, P. L. Burn and P. Meredith, *Polym. Chem.*, 2011, **2**, 2360.
8 N. Niamnont, W. Siripornnoppakhun, P. Rashatasakhon and M. Sukwattanasinitt, *Org. Lett.*, 2009, **11**, 2768.
9 (*a*) S. Kajigaeshi, T. Kakinami, M. Moriwaki, T. Tanaka, S. Fujisaki and T. Okamoto, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 439; (*b*) F. Liu, C. Tang, Q. Q. Chen, S. Z. Li, H. B. Wu, L. H. Xie, B. Peng, W. Wei, Y. Cao and W. Huang, *Org. Electron.*, 2009, **10**, 256.
10 (*a*) Y. T. Wu and J. S. Siegel, *Chem. Rev.*, 2006, **106**, 4843; (*b*) J. Mack, P. Vogel, D. Jones, N. Kavala and A. Sutton, *Org. Biomol. Chem.*, 2007, **5**, 2448.
11 L. Porres, O. Mongin, C. Katan, M. Charlot, T. Pons, J. Mertz and M. Blanchard-Desce, *Org. Lett.*, 2004, **6**, 47.
12 (*a*) A. K. Schrock and G. B. Schuster, *J. Am. Chem. Soc.*, 1984, **106**, 5234; (*b*) T. Romero, A. Caballero, A. Tarraga and P. Molina, *Org. Lett.*, 2009, **11**, 3466.
13 (*a*) T. J. Seiders, K. K. Baldridge and J. S. Siegel, *J. Am. Chem. Soc.*, 1996, **118**, 2754; (*b*) T. J. Seiders, E. Elliott, G. Grube and J. S. Siegel, *J. Am. Chem. Soc.*, 1999, **121**, 7804; (*c*) M. C. Stuparu, *Tetrahedron*, 2012, **68**, 3527.
14 (*a*) A. O. Doroshenko, A. V. Kirichenko, V. G. Miting and O. A. Ponomaryov, *J. Photochem. Photobiol., A*, 1996, **94**, 15; (*b*) R. Karpicz, S. Puzinas, S. Krotkus, K. Kazlauskas, S. Jursenas, J. V. Grazulevicius, S. Grigalevicius and V. Gulbinas, *J. Chem. Phys.*, 2011, **134**, 204508.
15 Computational methods and references in ESI†.
16 N. Niamnont, R. Mungkarndee, I. Techakriengkrai, P. Rashatasakhon and M. Sukwattanasinitt, *Biosens. Bioelectron*, 2010, **26**, 863.
17 M. E. Germain and M. J. Knapp, *J. Am. Chem. Soc.*, 2008, **130**, 5422.
18 F. Samain, S. Ghosh, Y. N. Teo and E. T. Kool, *Angew. Chem., Int. Ed.*, 2010, **49**, 7025.
19 K. Zhang, H. Zhou, Q. Mei, S. Wang, G. Guan, R. Liu, J. Zhang and Z. Zhang, *J. Am. Chem. Soc.*, 2011, **133**, 8424.