Organic nanofibrils based on linear carbazole trimer for explosive sensing

Chengyi Zhang, Yanke Che,* Xiaomei Yang, Benjamin R. Bunes and Ling Zang*

Department of Materials Science and Engineering, the University of Utah, Salt Lake City, UT, 84108, USA. Fax: (+1)801-585-0625; Tel: (+1)801-587-1551; E-mail: ykminmin@gmail.com, lzang@eng.utah.edu .

1. Experimental details

Materials and Characterization: 2,4-dinitrotoluene (DNT, 97%) and 2,4,6-trinitrotoluene (TNT, 99%) were purchased from Fisher and Chemservice, respectively. All other molecules and solvents (HPLC or spectroscopic grade) were purchased from Fisher or Aldrich and used as received.

UV-vis absorption spectra and fluorescence spectra were measured on a PerkinElmer Lambda 25 spectrophotometer and LS 55 fluorometer, respectively. Fluorescence microscopy imaging was carried out with a Leica DMI4000B inverted microscope, with excitation at 365 nm. SEM measurement was performed with a FEI NanoNova 6300 microscope, and the samples were directly drop-cast on a silica substrate. X-ray diffraction was carried out with a Philips X'Pert XRD instrument. The time-dependent fluorescence quenching profile (Fig. 2b and Fig. 3b) was measured with an Ocean Optics USB4000 fluorometer. The fluorescence quenching by explosive vapor was monitored following similar methods previously developed in our lab.[1-2]

Synthesis of the carbaozle trimer: A solution of 2,7-dibromo-9-octyl-9H-carbazole (220 mg, 0.5 mmol), 9H-carbazole-2-boronic acid pinacol ester (880 mg, 1.5 mmol) and benzyltriethylammonium chloride (50 mg) in a mixture of toluene (20 mL) and aqueous K_2CO_3 (2M, 8mL) was degassed by three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (5 mg) was added under argon and degassed by three freeze-pump-thaw again. The mixture was refluxed for 24 h and the organic phase separated and evaporated. The product was purified by column chromatography (hexane/THF, 4:2) and dried in vacuum. A 220 mg (71%) yield of trimer carbazole was obtained as a light brown powder. ^{1}H NMR (THF-*d*8, 500 MHz): δ=10.33 (s, 2H), 8.15 (m, 4H), 8.07 (d, *J*=7.9, 2H), 7.82 (m, 4H), 7.6 (m, 4H), 7.43 (d, *J*=8.0, 2H), 7.34 (m, 2H), 7.15 (m, 2H), 4.56 (t, *J*=7.19, 2H), 1.99 (m, 2H), 1.29 (m, 10H), 0.83 (t, *J*=6.9, 3H). MALDI-TOF MS: *m*/*z* 609.33 (100%).

Fabrication of nanofibril films: 0.5 mL carbazole trimer solution (0.5 mM, in tetrahydrofuran) was dropped into 3 mL of hexane while stirring. A white floc (entangled nanofibrils) was formed immediately and suspended in the solution. To fabricate the nanofibril films, one drop of the nanofibril solution was cast onto a glass slide or silicon substrate, followed by drying in a vacuum oven for 30 minutes. For detection of nitroaromatic explosives (DNT and TNT), the films used are in the thickness of about 150 nm. For detection of nitromethane, the films in the thickness of about 300 nm were fabricated.

2. More figures

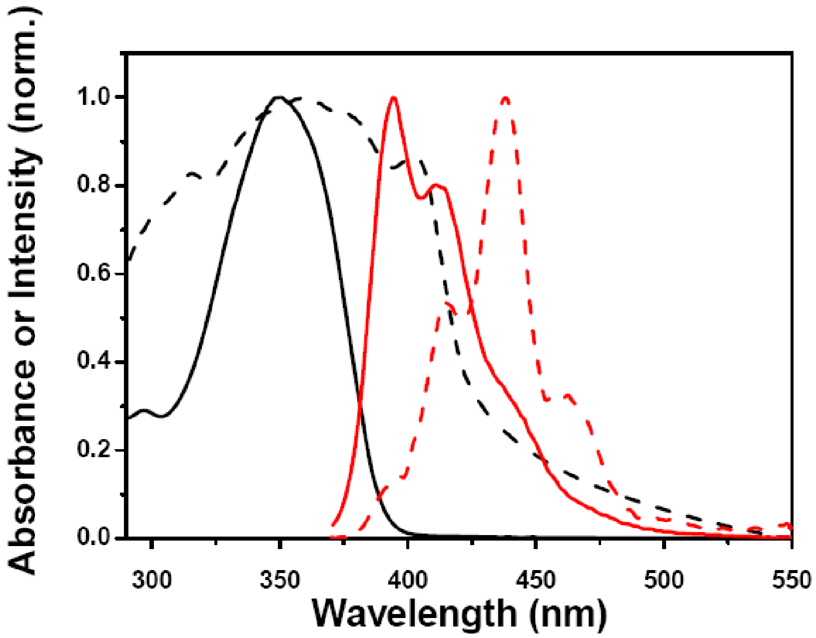

Fig. S1 The absorption (black) and fluorescence (red) spectra of the carbazole trimer in tetrahydrofuran solution (5 μM, solid) and nanofibril film deposited on glass (dashed). The fluorescence spectra were excited at 350 nm.

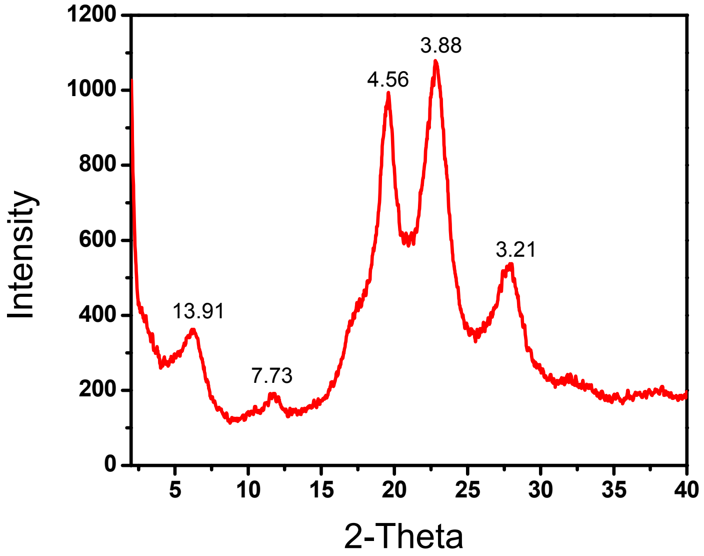

Fig. S2 XRD spectrum recorded from the nanofibrils. The d-spacings (Å) are labeled on the peaks.

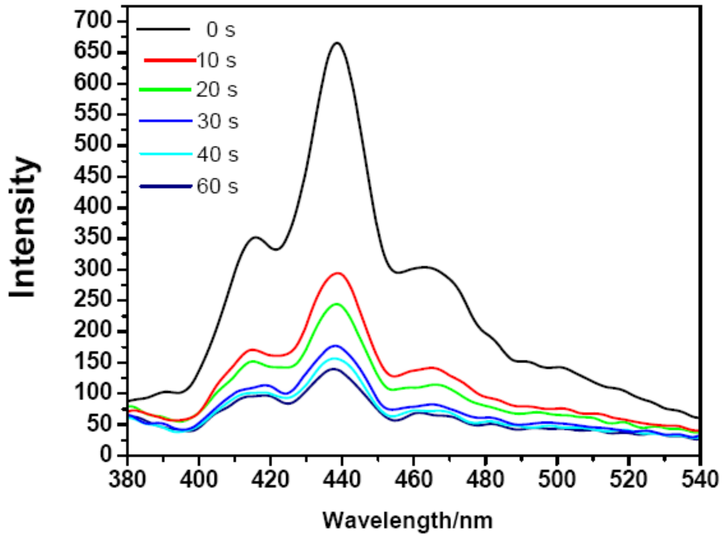

Fig. S3 Fluorescence spectra of the nanofibril film upon exposure to DNT saturated vapor (100 ppb) at various time intervals.

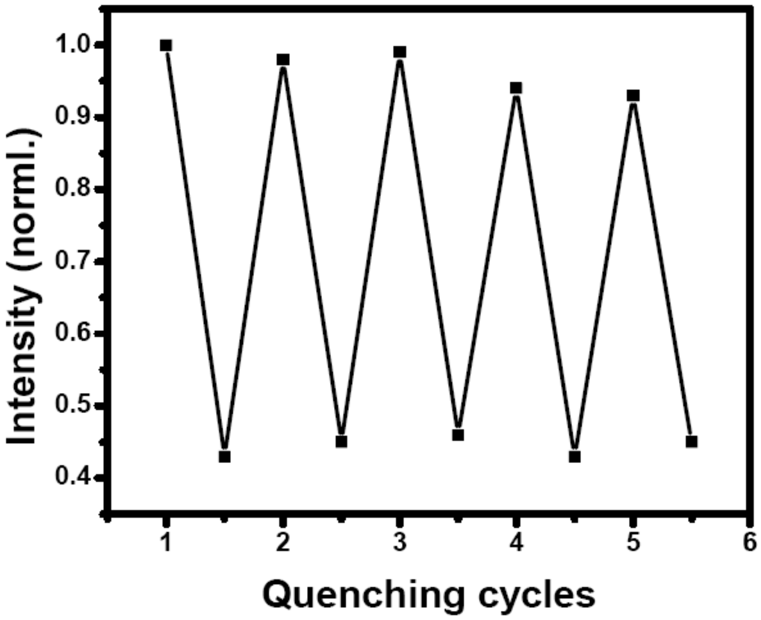

Fig. S4 Five continuous quenching-recovery cycles as performed for the nanofibril film upon exposure to DNT. The quenching was performed by exposing the film to a saturated vapor of DNT for 30 s and the fluorescence was recovered by heating the film at 50 °C in a vacuum oven for 10 min.

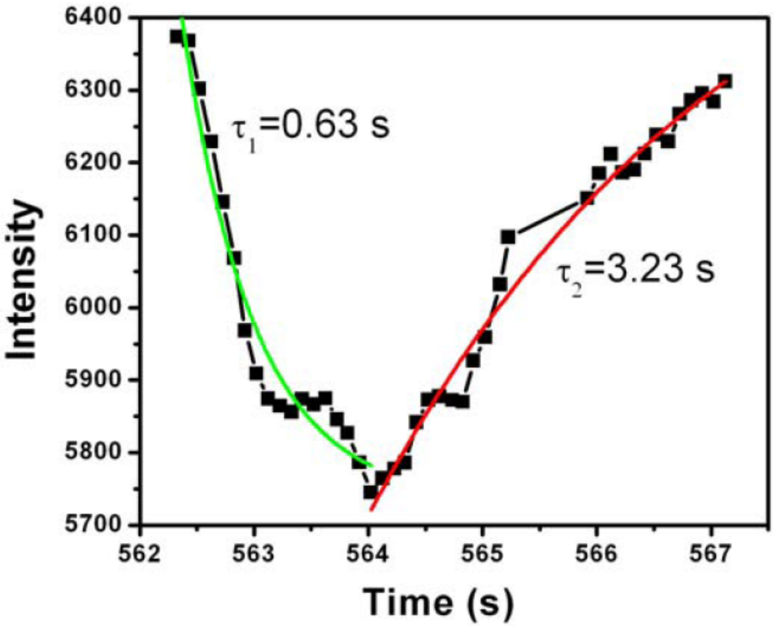

Fig. S5 Fitting the fluorescence quenching and recovery process into a single exponential kinetics.

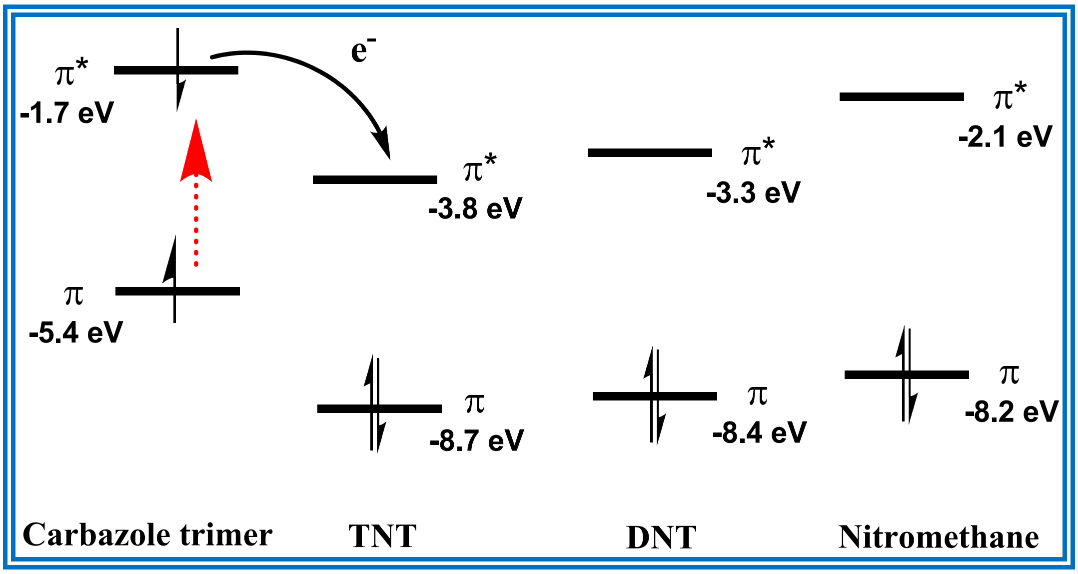

Fig. S6 Energy levels of HOMO (π) and LUMO (π*) orbitals of the carbazole trimer, TNT, DNT and nitromethane showing the favorable driving force of electron transfer from the photoexcited state of carbazole to TNT (2.1 eV), DNT (1.6 eV) and nitromethane (0.4 eV). Geometry optimization and energy calculation were performed with density-functional theory (B3LYP/6-311g**) using the Gaussian 03 package.

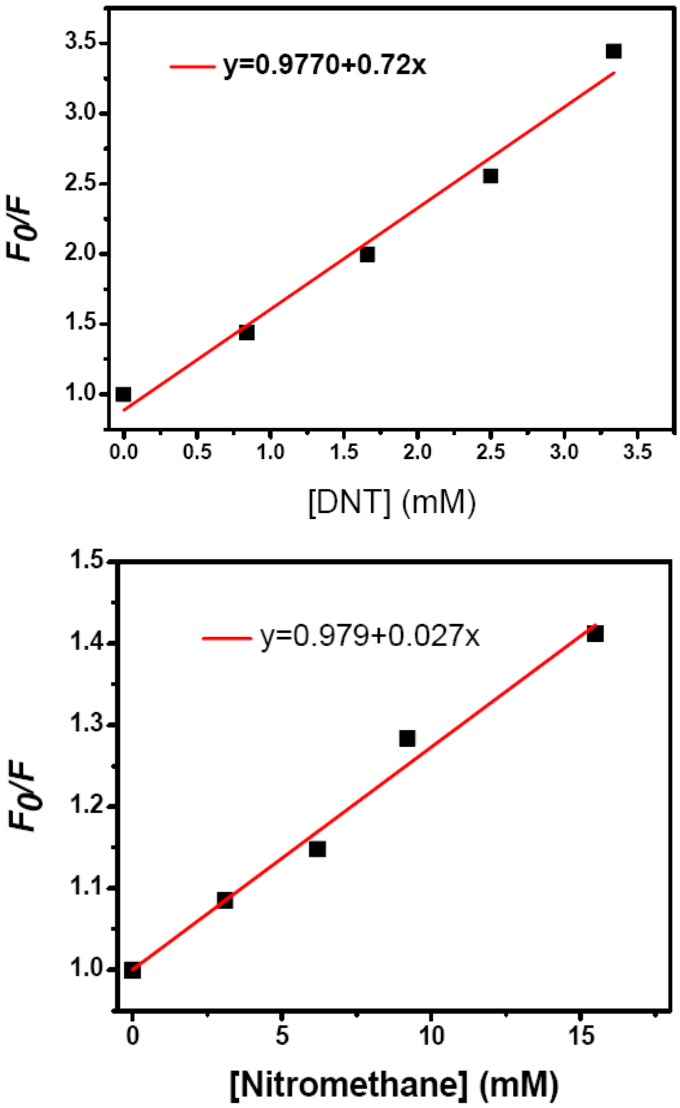

Fig. S7 Stern-Volmer plots for the fluorescence quenching of the carbazole trimer by DNT and nitromethane, giving quenching constants of 720 M^{-1} and 27 M^{-1}, respectively.

Reference:

1. T. Naddo, Y. Che, W. Zhang, K. Balakrishnan, X. Yang, M. Yen, J. Zhao, J. S. Moore and L. Zang, *J. Am. Chem. Soc.*, 2007, **129**, 6978-6979.
2. Y. Che, X. Yang, S. Loser and L. Zang, *Nano Lett.*, 2008, **8**, 2219-2223.