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Supplementary Information

Dual functional and multiple substituted fluorescent star-shaped POSS for a 1+1>2 explosive vapour detection

Yixun Gao,[a,b] Wei Xu[a,b], Xiangtao Zhang[a,b],Yanyan Fu[a], Defeng Zhu[a], Qingguo He[a] , Huimin Cao[a] , and Jiangong Cheng[a]

[a]State Key Lab of Transducer Technology, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Changning Road 865,Shanghai 200050, China. E-mail: hqg@mail.sim.ac.cn; jgcheng@mail.sim.ac.cn.

[b]University of the Chinese Academy of Sciences, Yuquan Road 19, Beijing,100039, China

Catalogue

1. Materials and Instruments

All chemicals and solvents were obtained from commercial sources and used as received without further purification. Polyhedral octavinylsilsesquioxane (purity, 95%) was bought from Aladdin Industrial Corporation. UV-Vis absorption, fluorescence analysis and lifetime measurements were obtained by HORIBA Fluoromax Plus spectrometer with time-correlated single-photon counting (TCSPC) device. Cyclic voltammetry curves were measured by electrochemistry workstation from Shanghai Chenhua Corporation.

2. Synthesis

Synthesis of POSS-5DOF

2-bromofluorene (20 mmol, 4.88 g) and tetrabutylammonium bromide (1.25 mmol, 0.4 g) were added to a flask with DMSO (40 mL) and 50% aqueous solution of NaOH (25 mL). Then 1-bromooctane (100 mmol, 19.3 g) was slowly added to the mixture. After stirred at 100 ºC for 12 hrs, the mixture was extracted by dichloromethane and water to obtain colorless oily **DOF-Br** (5.23 g) in a yield of 56%. ^{1}H NMR (500M, $CDCl_3$, ppm): δ 7.655 (t, 1H, J=7 Hz), 7.544 (d, 2H, J=7.5 Hz), 7.448 (s, 1H), 7.430 (d, 1H, J=2 Hz), 7.311 (s, 3H), 1.925 (q, 4H, J=10 Hz), 1.227-1.037 (m, 21H), 0.820 (t, 6H, J=14 Hz). ^{13}C NMR (500M, $CDCl_3$, ppm): 151.04, 147.16, 141.14, 140.23, 133.11, 130.62, 129.59, 126.78, 122.91, 121.15, 119.93, 52.27, 43.78, 43.69, 31.87, 29.91, 29.17, 24.42, 22.67, 14.06.

Polyhedral octavinylsilsesquioxane (**POVS**) (1.5 mmol, 0.95 g), **DOF-Br** (8 mmol, 3.75 g), and $Pd_2(dba)_3$ (0.3 mmol, 0.27 g) were placed in an oven-dried round bottom Schlenk flask. A mixture of freshly dried dioxane (40 mL), N,N-dicyclohexylmethylamine (72 mmol, 15.5 mL) and Tri-*tert*-butylphosphine (1 M solution, 0.75 mmol, 0.75 mL) was added to the degassed flask. The reddish brown mixture was stirred at 85 ºC for 48 hrs. After cooling to room temperature, it was then filtered and the filtrate was poured into methanol. The precipitate was

collected and purified by column chromatography using dichloromethane and petroleum ether as eluent with a ratio of 1:4. After drying, 1.4 g colorless gelatinous **POSS-5DOF** was obtained in a yield of 36%. ^{1}H NMR (500M, $CDCl_3$, ppm): δ 7.670 (s, 8H), 7.529-7.407 (m, 12H), 7.312 (d, 12H, J=7.5 Hz), 6.389-6.164 (m, 10H), 1.970 (s, 16H), 1.257-0.953 (m, 91H), 0.882-0.752 (m, 32H). MALDI-MS calcd. for $C_{161}H_{224}O_{12}Si_8$: 2576.2; found: 2600, 2988. ^{13}C NMR (500M, $CDCl_3$, ppm): 151.18, 149.76, 142.28, 140.63, 137.05, 136.36, 129.10, 127.30, 126.79, 126.37, 122.90, 121.09, 121.00, 119.87, 119.72, 116.36, 55.06, 40.41, 31.77, 30.00, 29.19, 23.72, 22.57, 14.05.

Synthesis of POSS-5PT

4-(6-bromopyrenyl)-triphenylamine (**PT-Br**) was synthesized by a 1:1 feed ratio of 1,6-dibromopyrene and 4-(N,N-diphenyl)aminophenylboronic acid pinacol ester through Suzuki cross-coupling reaction, using tetrakis(triphenylphosphine) palladium ($Pd(PPh_3)_4$) as catalyst. ^{1}H NMR (500M, $CDCl_3$, ppm): δ 8.29 (d, 1H, J=9.4 Hz), 8.19 (t, 1H, J=5 Hz), 8.16 (d, 2H, J=9.3 Hz), 8.08 (s, 2H), 8.04 (d, 1H, J=13.8 Hz), 8.00 (t, 2H, J=6 Hz), 7.56 (d, 2H, J=8.5 Hz), 7.32 (t, 4H, J=7.5 Hz), 7.24 (t, 6H, J=9 Hz), 7.07 (t, 2H, J=7.5 Hz). ^{13}C NMR (500M, $CDCl_3$, ppm): 137.46, 134.99, 131.52, 131.37, 131.02, 130.38, 129.36, 128.45, 127.63, 127.44, 127.33, 127.28, 125.98, 125.42, 125.02, 124.73, 124.70, 124.61, 123.29, 123.05.

Similar methods were used for Heck reaction. **POVS** (1.5 mmol, 0.95 g), **PT-Br** (8 mmol, 4.15 g), and $Pd_2(dba)_3$ (0.3 mmol, 0.27 g) were placed in an oven-dried round bottom Schlenk flask. A mixture of freshly dried dioxane (40 mL), N,N-dicyclohexylmethylamine (72 mmol, 15.5 mL) and Tri-*tert*-butylphosphine (1 M solution, 0.75 mmol, 0.75 mL) was added to the flask. After stirring for 48 hrs at 85 ºC, the product was filtered and purified by column chromatography. 1.8 g yellow powdered **POSS-5PT** was obtained in a yield of 47%. ^{1}H NMR (500M, $CDCl_3$, ppm): δ 6.98 (s, 4H), 5.01 (s, 2H), 9.21-7.62 (m, 25H), 7.62-6.49 (m, 67H), 6.49-5.82 (m, 3H). ^{13}C NMR (500M, $CDCl_3$, ppm): 137.28, 134.59, 131.24, 131.13, 131.02, 130.33, 129.34, 128.47, 127.40, 127.32,

127.18, 126.02, 125.23, 125.02, 124.66, 124.60, 122.98, 122.75. MALDI-MS calcd. for $C_{187}H_{131}N_5O_{12}Si_8$: 2861.8; found: 2847, 3289, 3732.

Synthesis of P5F1PT

Similar methods were used for Heck reaction. **POSS-5DOF** (0.2 mmol, 514 mg), **PT-Br** (0.2 mmol, 105 mg), and $Pd_2(dba)_3$ (0.008 mmol, 7.2 mg) were placed in an oven-dried round bottom Schlenk flask. A mixture of freshly dried dioxane (15 mL), N,N-dicyclohexylmethylamine (1.6 mmol, 0.34 mL) and Tri-*tert*-butylphosphine (1 M solution, 16 µmol, 16 µL) was added to the flask. After stirring for 48 hrs at 85 ºC, the product was filtered and purified by column chromatography. 132 mg yellow powdered **P5F1PT** was obtained in a yield of 22%. ^{1}H NMR (500M, $CDCl_3$, ppm): δ 8.454-8.377 (m, 2H), 8.338-8.264 (m, 1H), 8.163-8.127 (m, 1H), 8.032-7.837 (m, 4H), 7.728-7.652 (m, 8H), 7.617-7.437 (m, 11H), 7.361-7.205 (m, 28H), 7.098-7.041 (m, 1H), 6.754-6.051 (m, 8H), 2.066-1.803 (m, 12H), 1.505 (s, 2H), 1.258 (s, 3H), 1.218-0.830 (m, 64H), 0.827-0.690 (m, 22H), 0.667-0.468 (m, 16H). ^{13}C NMR (500M, $CDCl_3$, ppm): 151.20, 149.81, 147.79, 142.31, 140.64, 136.41, 131.38, 129.36, 127.31, 126.80, 124.63, 123.28, 123.08, 122.92, 119.88, 55.09, 40.42, 31.78, 30.02, 29.20, 29.13, 23.73, 22.58, 22.53, 14.06. MALDI-MS calcd. for $C_{195}H_{245}NO_{12}Si_8$: 3019.8; found: 2632, 3021, 3411.

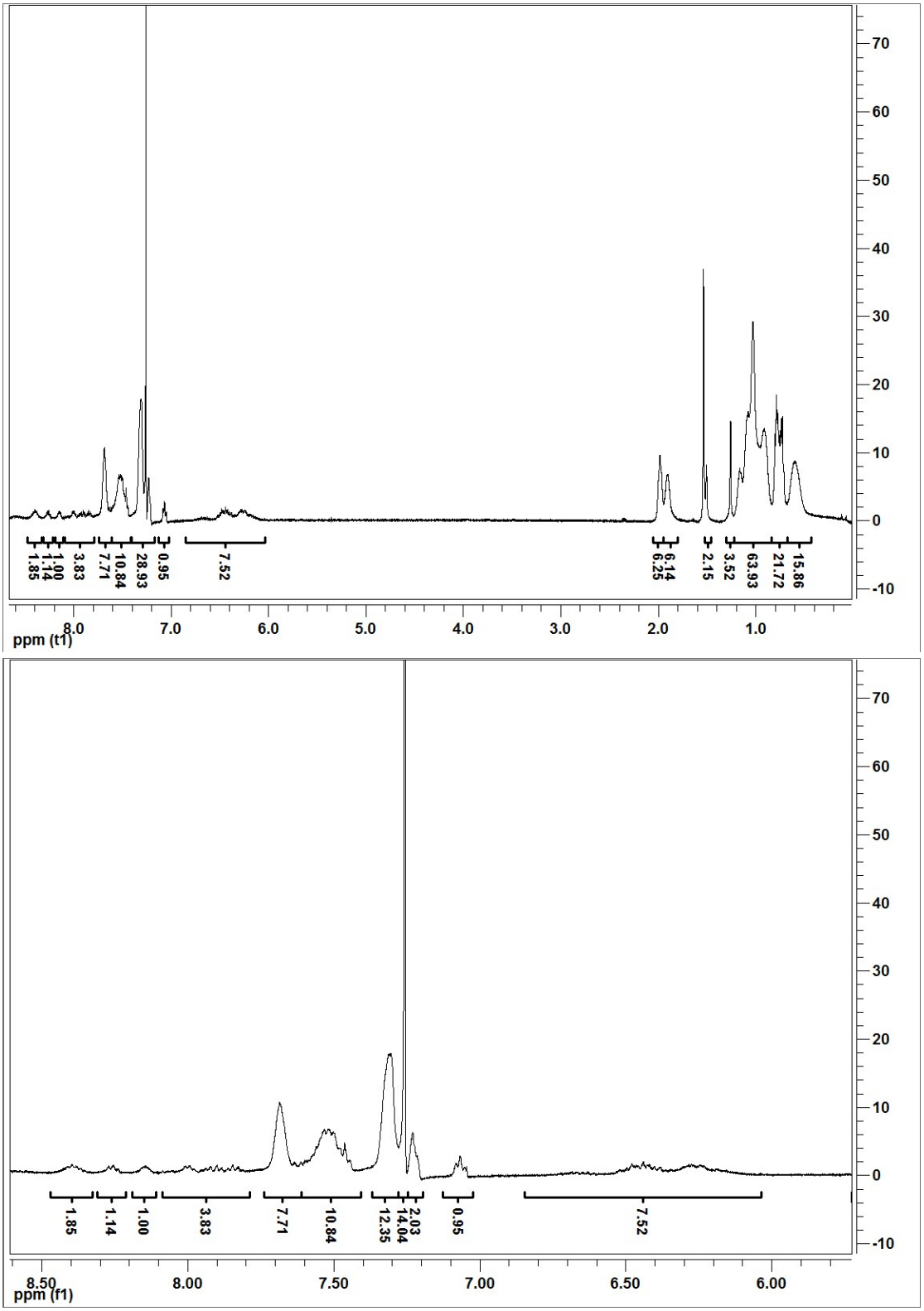

Fig. S1 ^{1}H NMR spectrum of **P5F1PT**.

As showed in the figure, the 8H from 7.7 to 8.5 ppm were H atoms from di-substituted pyrene in PT unit. The 48H from 7.05 to 7.75 were H atoms from TPA and fluorene in DOF, and 8H from 6.04 to 6.85 were H atoms from vinyl on POVS. As mono-substituted TPA has 14 H atoms, 48-

14=34 H atoms would be from fluorenes. One fluorene in DOF has 7 aromatic H atoms, thus 34 H could prove that the ratio of DOF: PT was about 5:1. The ^{1}H-NMR proved that the as-synthesized is mainly **P5F1PT.**

3. Mass spectrum

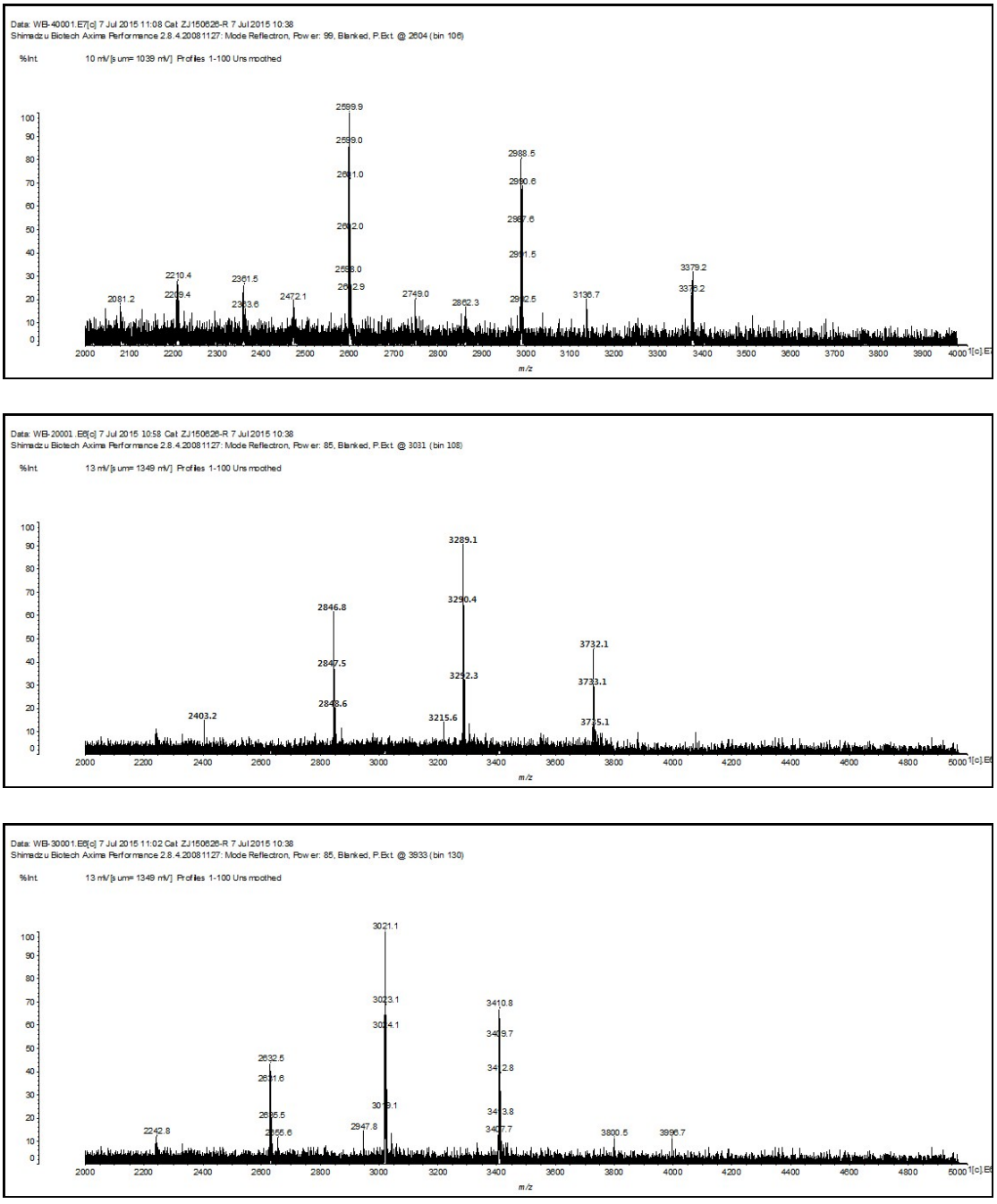

Fig. S2 Mass spectrum of **POSS-5DOF** (upper), **POSS-5PT** (mid) and **P5F1PT** (below).

4. Cyclic voltammetry curves

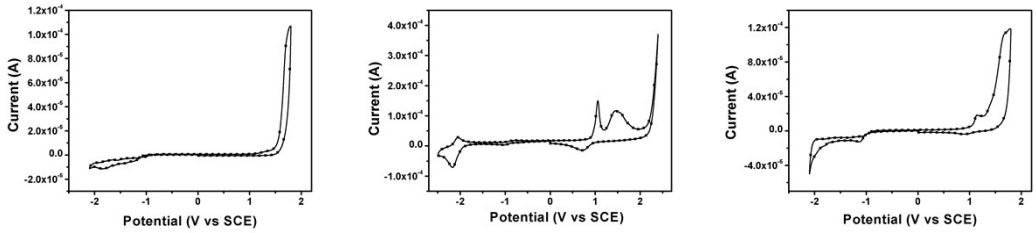

Fig. S3 Cyclic voltammetry curves of **POSS-5DOF** (left), **POSS-5PT** (mid) and **P5F1PT** (right).

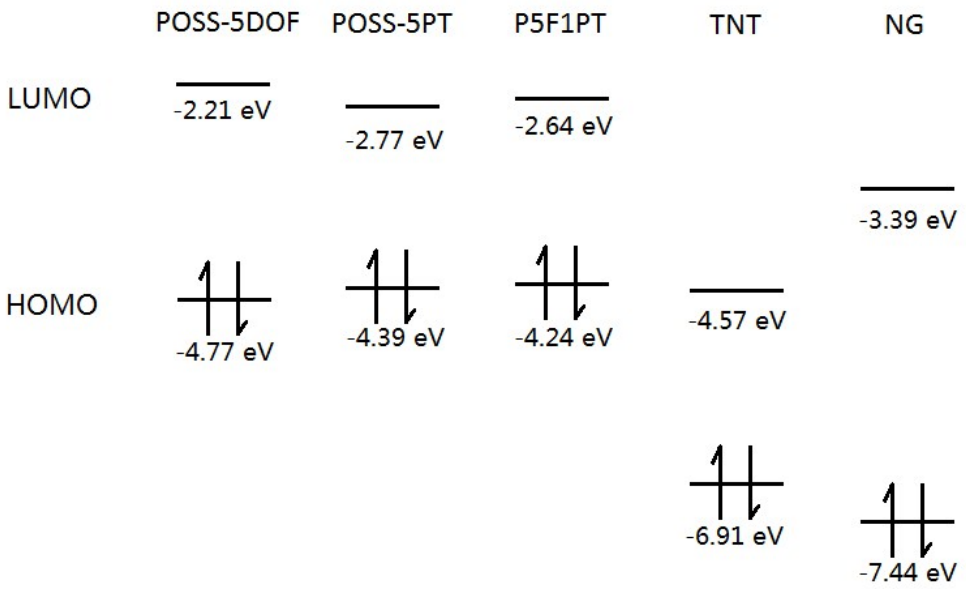

Fig. S4 HOMO and LUMO level of **POSS-5DOF**, **POSS-5PT**, **P5F1P,** TNT and NG.

Schematic of the HOMO and LUMO level of three POSS molecules and two explosive molecules with relative position were shown as above. The energy level of TNT and NG was obtained by reference.[1] LUMO level of TNT and NG are both lower than **P5F1PT**, which could prove the feasibility of PET mechanism for fluorescence quenching.

5. Orbital schematics calculated by Materials Studio

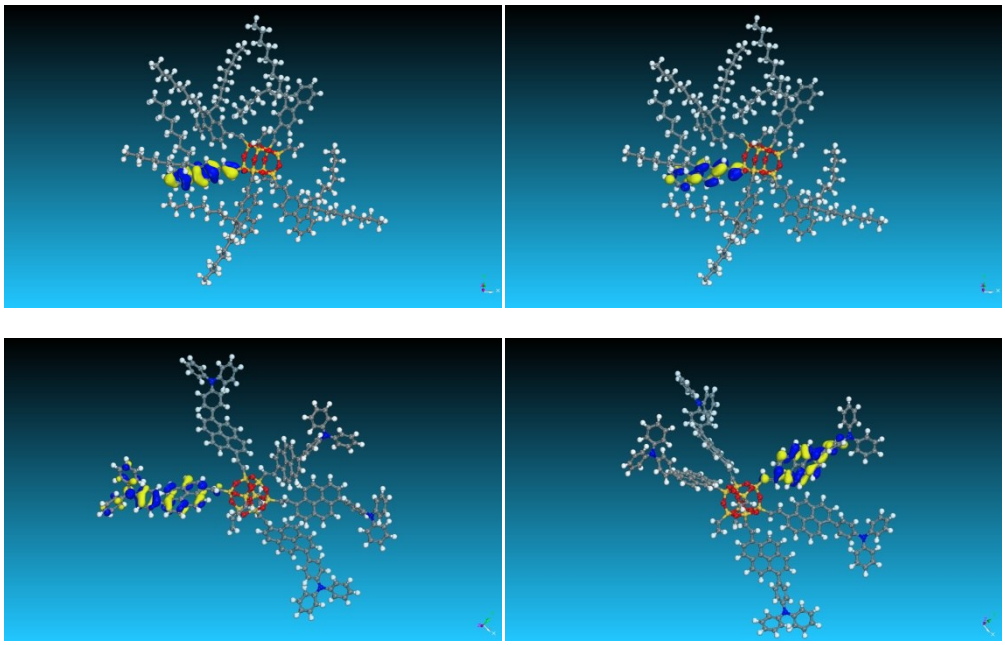

Fig. S5 Orbital schematics of **POSS-5DOF** (HOMO: upper left, LUMO: upper right) and **POSS-5PT** (HOMO: below left, LUMO: below right).

Orbital calculation of molecules was carried out by Materials Studio version 8.0 software using Geometry Optimization and Energy calculation tasks in DMol^3 module (Accelrys Software, Inc.). The optimization used a COMPASS II forcefield with atom-based summation for both the electrostatic and van der Waals parameters. Energy calculation used LDA and PWC as functional parameters.

6. Fluorescence Quenching Experiment

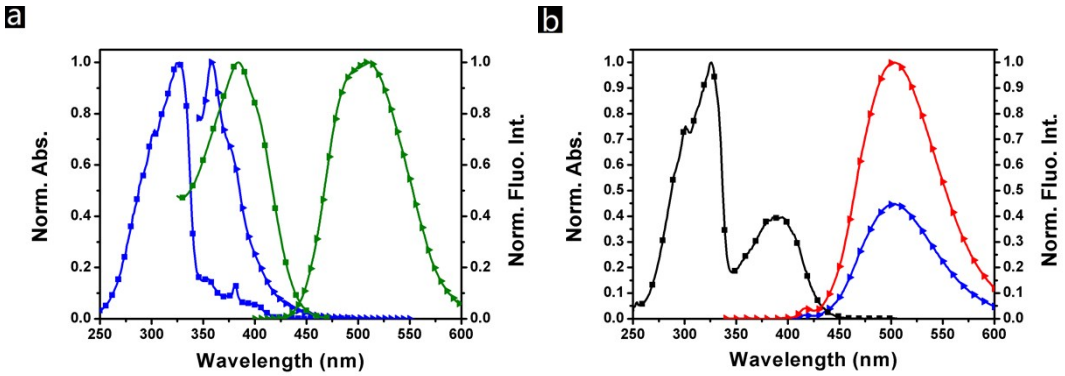

Fig. S6 (a) Absorption and fluorescence spectra of **POSS-5DOF** (blue) and **POSS-5PT** (green). (b) The absorption

spectra (black) and the emission spectra of **P5F1PT** under UV light of 330 nm (red) and 395 nm (blue). Both spectra were measured under THF solution at a concentration of 1×10^{-5} M.

7. Scanning Electron Microscope analysis

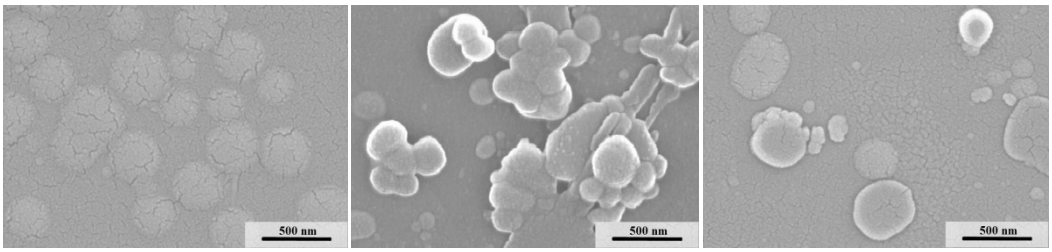

Fig.S7 SEM images of **POSS-5DOF** (left), **POSS-5PT** (mid), and **P5F1PT** (right). All the films were spin coated from their THF solutions with a concentration of 4×10^{-5} mol/L.

8. Fluorescence Quenching Experiment

The fluorescence quenching experiments of the sensing films towards explosive vapors were conducted as follows: a small amount of explosives or interferents (3 mg for solid or 3 μL for liquid) was placed in a 1-cm quartz cell with absorbent cotton covered to prevent direct contact of explosives and maintain a constant saturation vapor pressure. The sensing films were prepared by dip-coating a tetrahydrofuran solution of each material onto a 10 × 20 mm quartz plate and vacuum-dried for half an hour before use. With the sensing film inserted, the cell was placed in the fluorescence spectrometer. The emission data were collected at certain times in the wavelength region of 415-510 nm with an excitation wavelength of 330-395 nm, while the slit width of excitation and emission are 1 mm and 5 mm relatively.

9. Time-resolved PL decay measurements

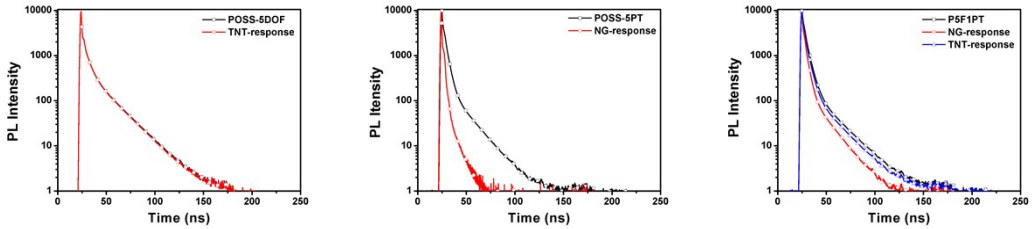

Fig.S8 Fluorescence lifetime of **POSS-5DOF** (left), **POSS-5PT** (mid) and **P5F1PT** (right) before and after response to saturated TNT and NG vapor for 300 s in room temperature.

As the products of three molecules consisted of several components, all the lifetime measurements were carried out with a triple-exponential fit. The detail data were listed below.

	Exp 1	Exp 2	Exp 3
POSS-5DOF	4.8 ns	20.4 ns	0.35 ns
Reponse to TNT	4.8 ns	20.1 ns	0.36 ns
POSS-5PT	3.1 ns	16.5 ns	0.55 ns
Reponse to NG	1.5 ns	7.8 ns	0.097 ns
P5F1PT	4.2 ns	19.9 ns	1.1 ns
Reponse to TNT	3.9 ns	18.9 ns	0.9 ns
Reponse to NG	3.1 ns	15.2 ns	0.6 ns

Table S1 Fluorescence lifetime of three POSS materials before and after response to TNT and NG by a triple-exponential fit.

References

1. S. J. Toal and W. C. Trogler, *Journal Of Materials Chemistry*, 2006, **16**, 2871-2883.