Supporting Information (SI) for:

New insights into the sensing mechanism of a phosphonate pyrene chemosensor for TNT

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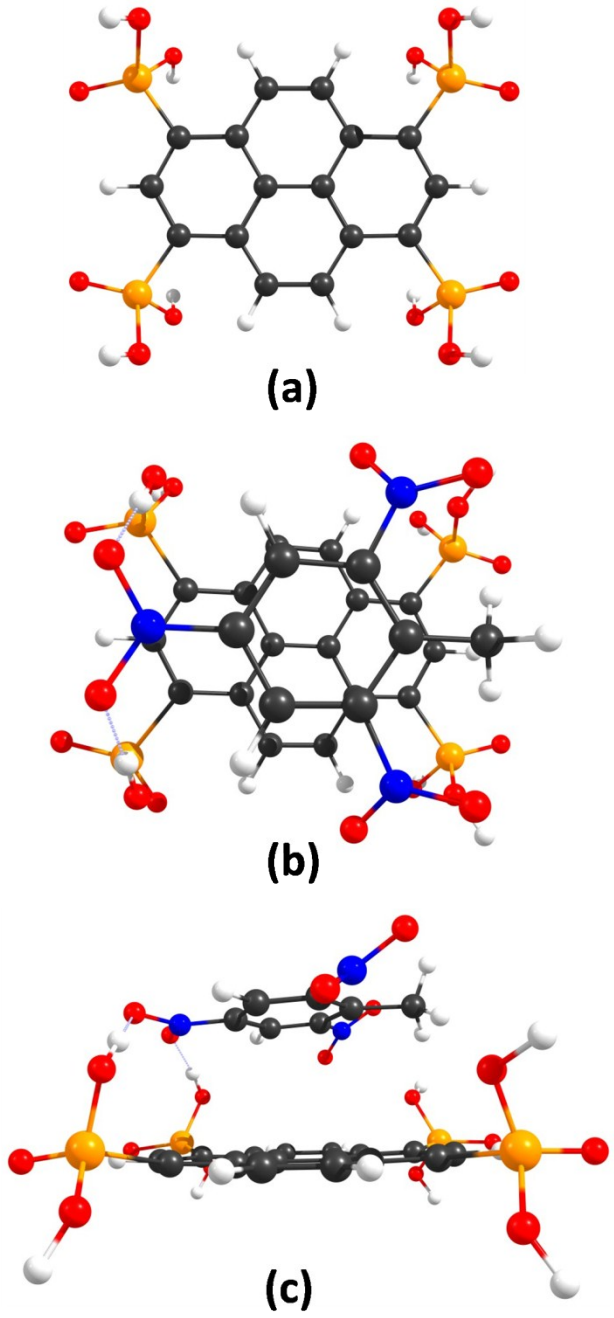

Figure S1. Geometric structures of optimized compounds (a) PO, (b) front view of PO-TNT and (c) side view of PO-TNT in S_1 state.

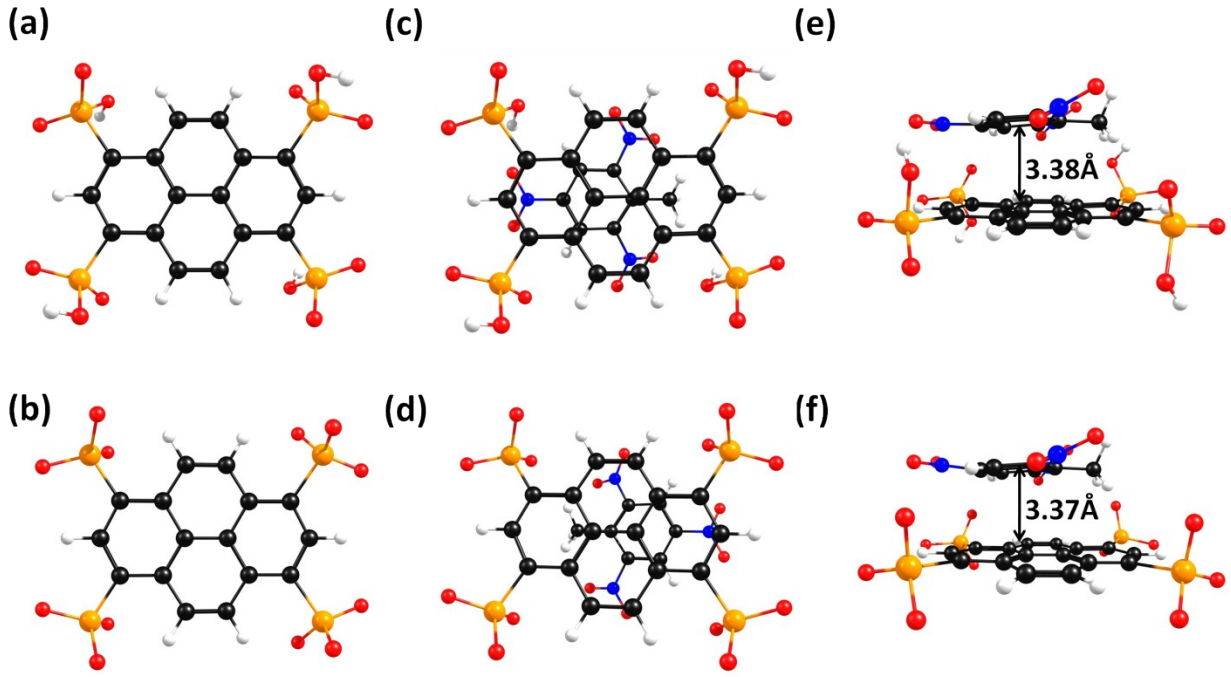

Figure S2. Geometric structures of optimized compounds (a) PO1, (b) PO2, (c) PO1-TNT, (d) PO2-TNT, (e) side view of PO1-TNT and (f) side view of PO2-TNT on ground state. The primary plane distances are marked in the figure.

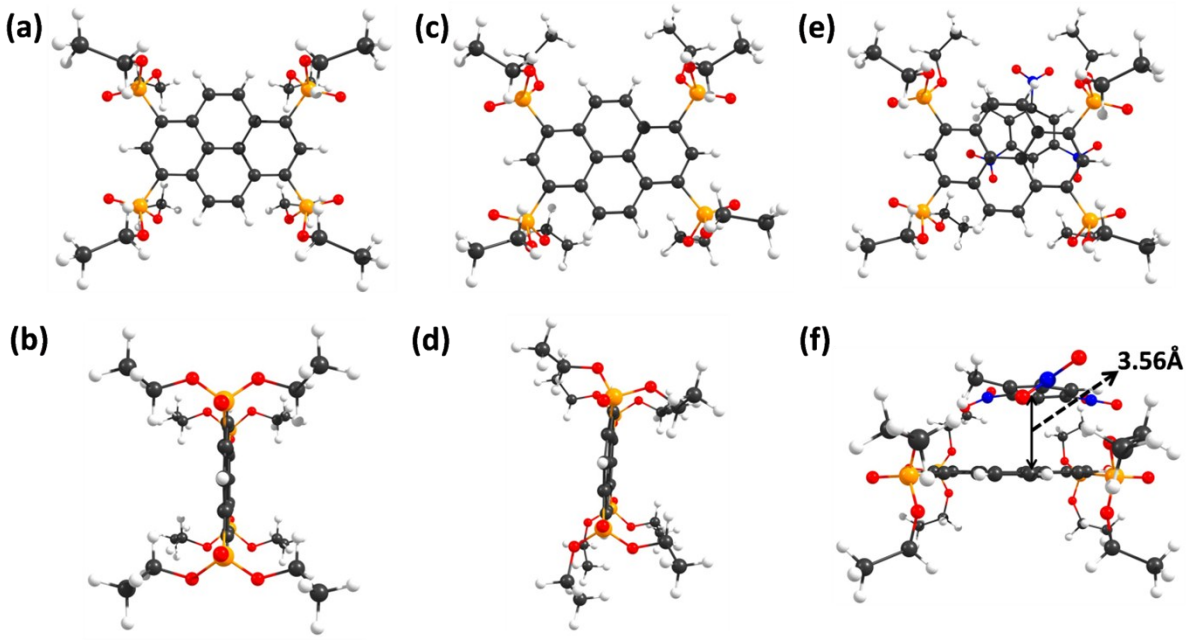

Figure S3. Geometric structures of optimized compounds (a) PE, (b) side view of PE, (c) PE-in-PETNT, (d) side view of PE-in-PETNT, (e) PE-TNT and (f) side view of PE-TNT on ground state. The primary plane distance is marked in the figure.

Table S1. The Gibbs free energy data of PE, PE-in-PETNT, PO and PO-in-POTNT in S_0 state.

	Raw Energy (a.u.)	Relative Energy (kcal/mol)
PE	-3515.078864	0
PE-in-PETNT	-3515.075239	2.27[a]
PO	-2886.456959	0
PO-in-POTNT$^+$	-2886.457447	-0.31[b]

[a] Relative energy compared with PE. [b] Relative energy compared with PO.

Table S2. The detailed theoretical and experimental electronic spectra data for PO1, PO2, PO1-TNT and PO2-TNT.

	Electronic transition	Wave length (nm)	Energy (ev)	f[a]	Contrib[b]	CI[c]	exp[d] (nm)
PO1							
Absorption	$S_0 \rightarrow S_1$	351.27	3.53	0.7662	H→L	0.96	375
Emission	$S_1 \rightarrow S_0$	367.32	3.38	1.1416	L→H	0.98	406
PO1-TNT							
Absorption	$S_0 \rightarrow S_5$	353.15	3.51	0.4965	H→L+3	0.69	
PO2							
Absorption	$S_0 \rightarrow S_1$	354.53	3.50	0.7810	H→L	0.96	375
Emission	$S_1 \rightarrow S_0$	370.30	3.35	1.1637	L→H	0.97	406
PO2-TNT							
Absorption	$S_0 \rightarrow S_{13}$	358.19	3.46	0.4247	H→L+1	0.70	

[a] Oscillator strength. [b] H, highest occupied molecular orbital (HOMO) and L, lowest unoccupied molecular orbital (LUMO). [c] The CI coefficients are in absolute values. [d] The experimental electronic spectra data are from Ref. 26.

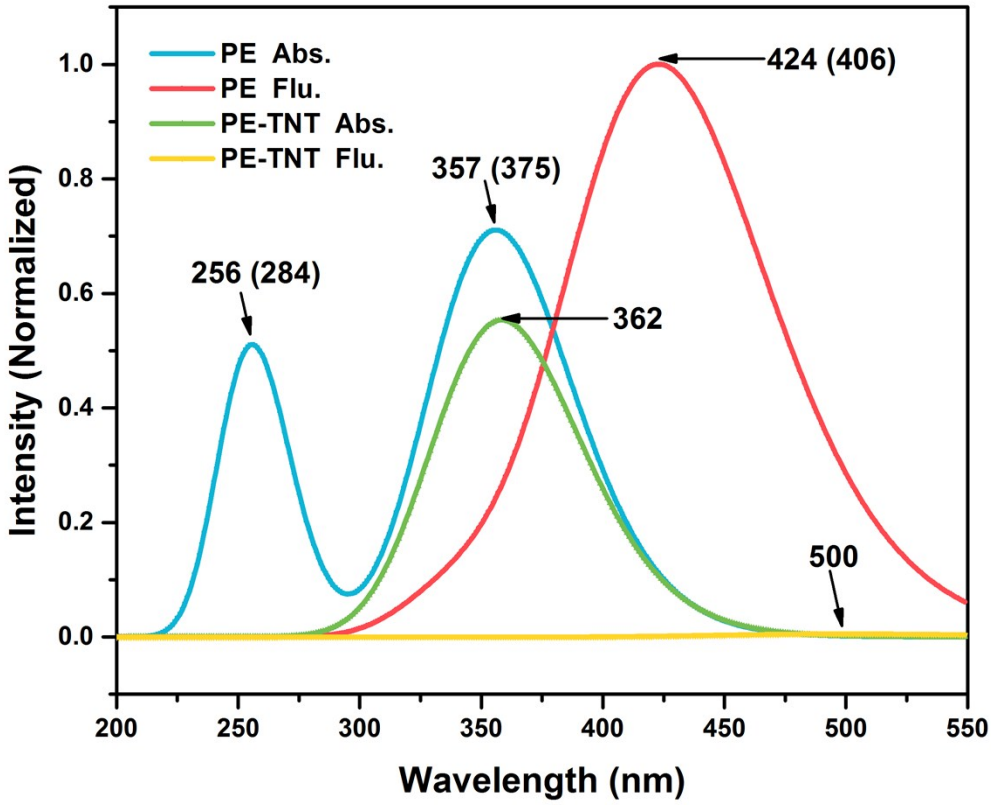

Figure S4. The calculated electronic spectra of PE and PE-TNT. The primary wavelengths (nm) of absorption and emission are marked and corresponding experimental values are given in the parenthesis.

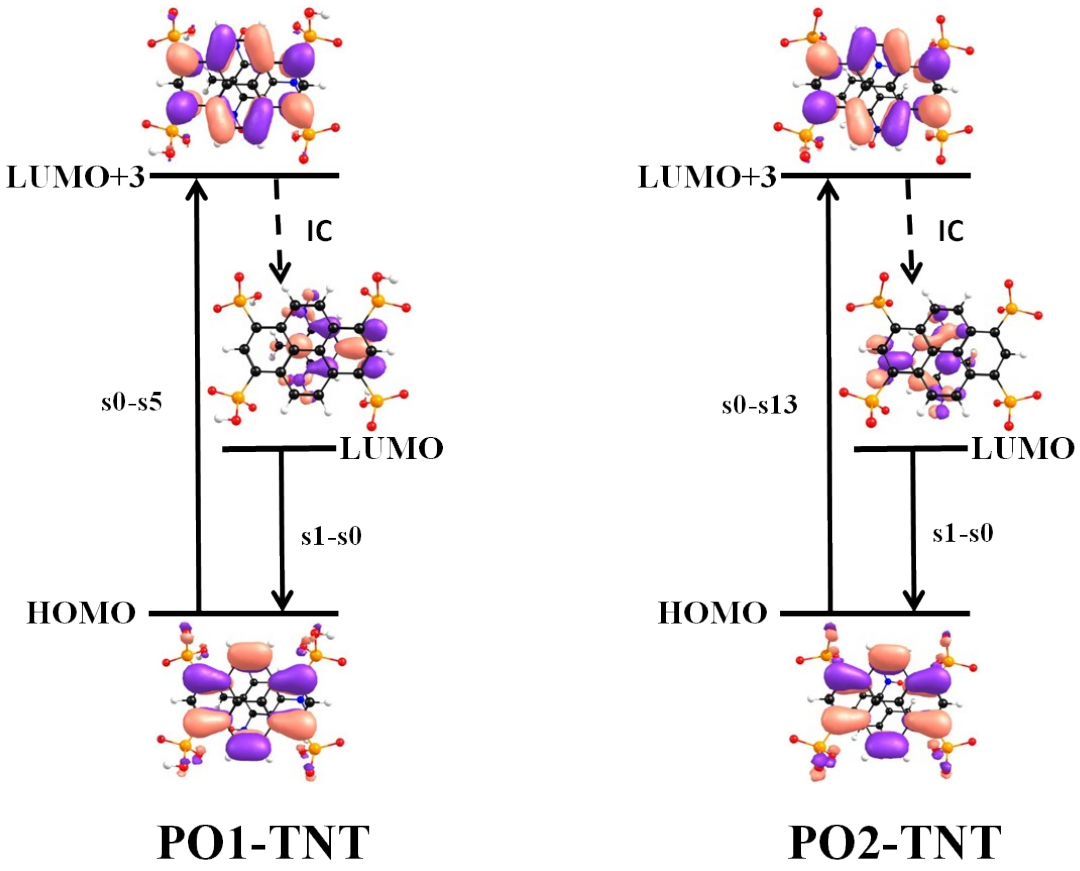

Figure S5. Scheme of the sensing mechanisms and relevant frontier molecular orbitals for PO1-TNT (left) and PO2-TNT (right).

Table S3. Raw energy data related to the calculation of charge transfer rate.

	Energy (a.u.)
PO*	-2885.96023842
TNT	-884.747055012
PO*···TNT	-3770.707293432
PO^{+}	-2885.84398224
TNT^{-}	-884.888998441
$PO^{+}\cdots TNT^{-}$	-3770.732980681
$[PO^*]^{+}$	-2885.83670527
$[TNT]^{-}$	-884.879346871
$[PO^*]^{+}\cdots[TNT]^{-}$	-3770.716052141
E_{L+1}	-0.0853
E_L	-0.0871