Three independent channels nanohybrids as fluorescent probes

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Supplementary information

Synthesis of trinitrotoluene (TNT)
TNT synthesis was performed following the procedure described in the literature.[1,2] Briefly, fuming sulfuric acid 30% (1.95 mL) was added in a three-necked flask (25 mL), and was cooled down to 0 °C in an ice-water bath. Then nitric acid 100% (0.6 mL) is add drop by drop under magnetic stirring, taking care that the reaction temperature does not exceed 15 °C. Subsequently 2,4-DNT (0.854 g) was added to the acid mixture, and the temperature was slowly increased to 90 °C, and allowed to stir 2 hours at this temperature. After, the reaction was allowed to cool (at 30 ºC) and was add to deionized water (50 mL), and extracted in a separator funnel with dichloromethane. The extracts were dried with $MgSO_4$, and the solvent was evaporated under vacuum. Yellow solid was obtained with a yield of 70 %. The solid was recrystallized in chloroform-ethanol mixture, to give a yellow crystalline solid.

1. W. H. Dennis, D. H. Rosenblatt, W. G. Blucher and C. L. Coon, *Journal of Chemical & Engineering Data*, 1975, **20**, 202-203.
2. R. C. Dorey and W. R. Carper, *Journal of Chemical & Engineering Data*, 1984, **29**, 93-97.

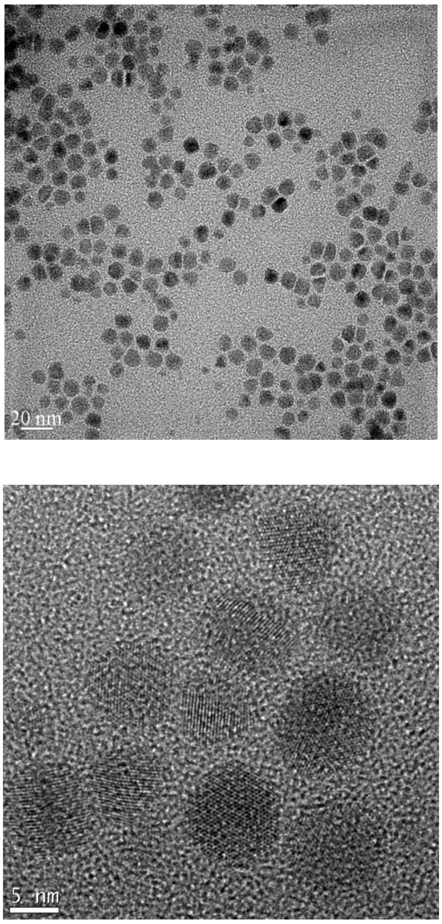


Figure S1. HRTEM images of CS@Py, diameter 8.4 ± 1.5 nm. Scale bar: a) 20 nm and b) 5 nm.

Table S1. PL data of CS, CS@PY and PySH in tetrahydrofuran at room temperature

	λ_{em}/nm[a]	**Φ_F**[b]	**τ_1/ns (A_1%)**[c]	**τ_2/ns (A_2%)**[c]	**$\tau_{average}$/ns**[e]	***Kk_r (s^{-1})***	***k_{nr} (s^{-1})***
CS	640	**37.7**	45.5 (53)	16.0 (47)	**38.4**	**9.82 10^6**	**16.2 10^6**
PySH	397		94.7 (100)[d]				
	398		87.4 (36)	15.9 (64)			
	480		53.3 (100)	17.3 (-112)			
CS@PY	640	**21.0**	43.1 (46)	11.8 (56)	**35.3**	**5.95 10^6**	**22.4 10^6**

[a]λ_{exc}= 340 nm. [b] Photoluminescence quantum yield. [c] Relative contribution to the biexponential fit. [d] Monoexponential fit. [e] Average lifetime, calculate as τ average= $\Sigma A_i \tau_i^2/\Sigma A_i \tau_i$

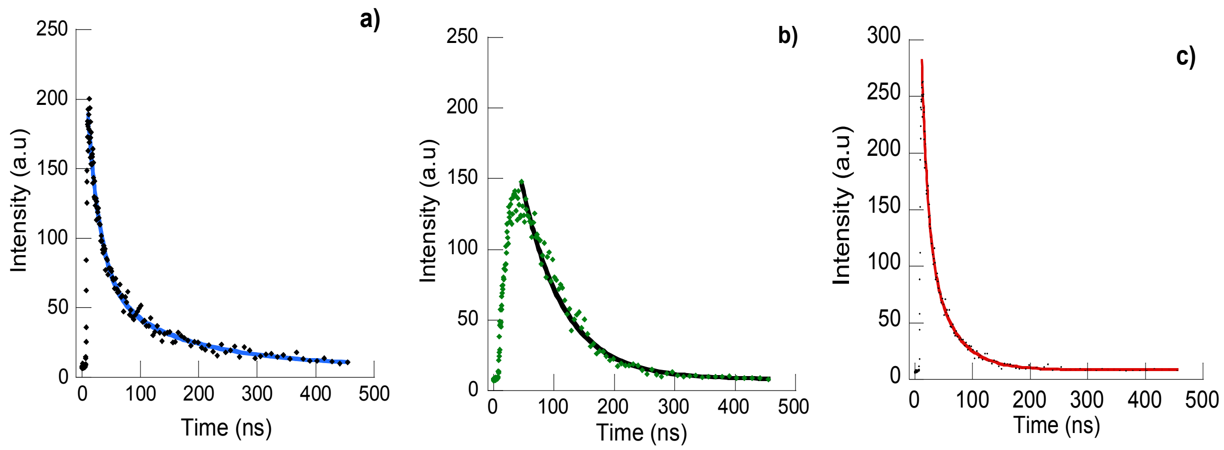
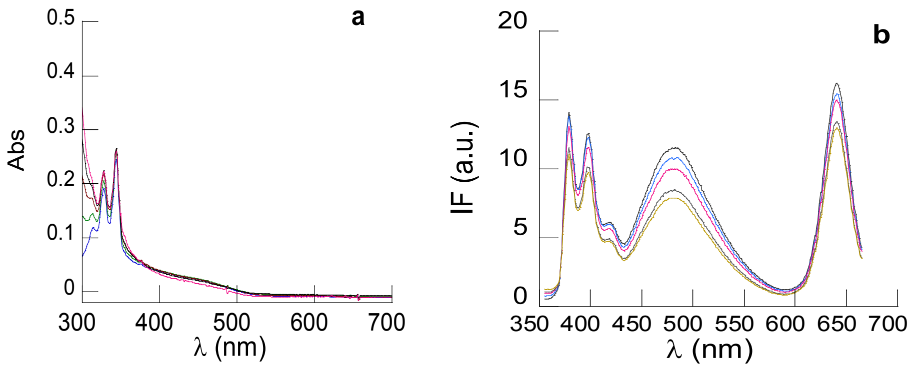
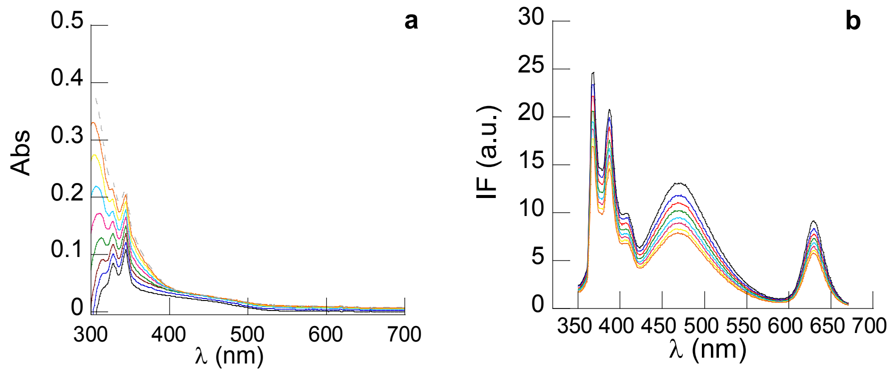


Figure S2: Kinetic decay traces and their fitting to exponential functions of time for the emissive species of CS@Py in THF (λ_{exc}= 340 nm): a) M* (λ_{em}= 397 nm), b) E* (λ_{em}= 480 nm), and c) CS*.

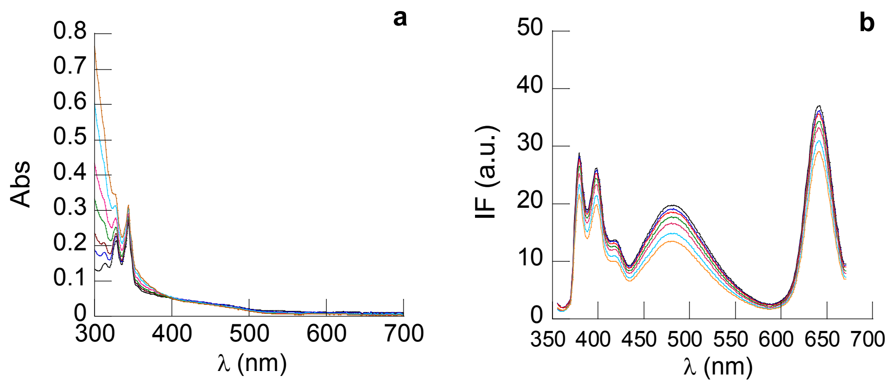
NB



2-NT



3-NT



4-NT

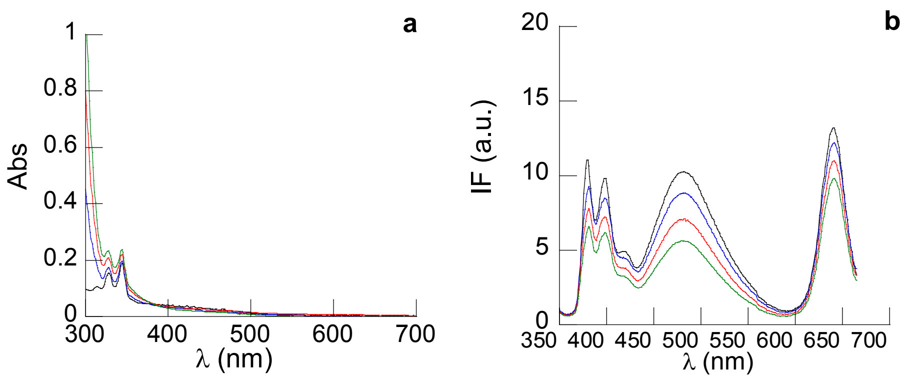
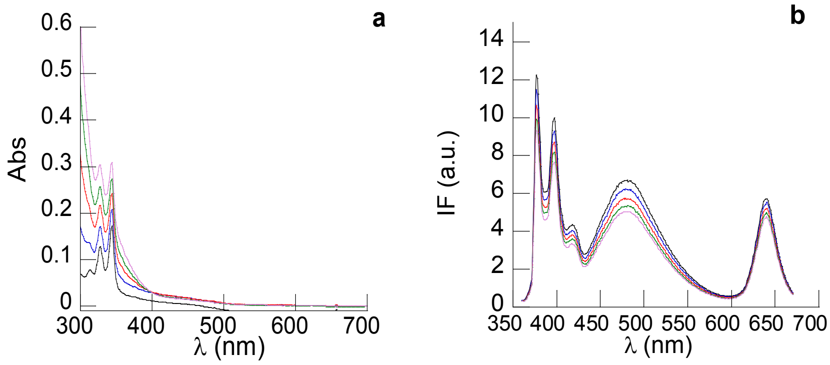


Figure S3: a) absorption and b) emission spectra (λ_{exc}= 340 nm) of CS@Py (5 nM) at different concentration of the NAC (0-0.25 mM) in THF, under N_2 atmosphere.

2,4-DNT



2,6-DNT

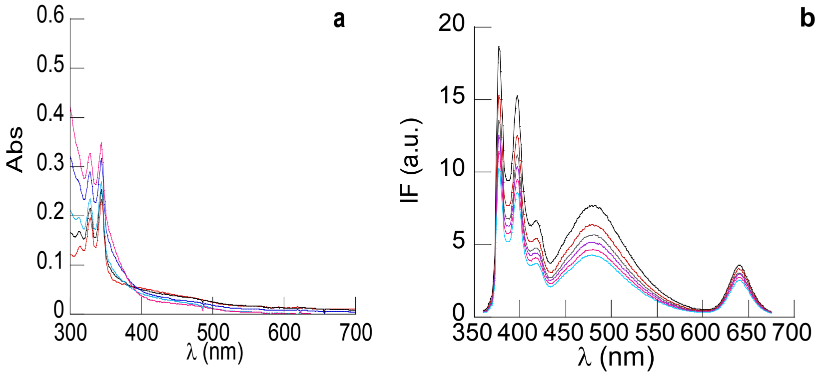


Figure S4: a) absorption and b) emission spectra (λ_{exc}= 340 nm) of CS@Py (5 nM) at different concentration of the NAC (0-0.25 mM) in THF, under N_2 atmosphere.

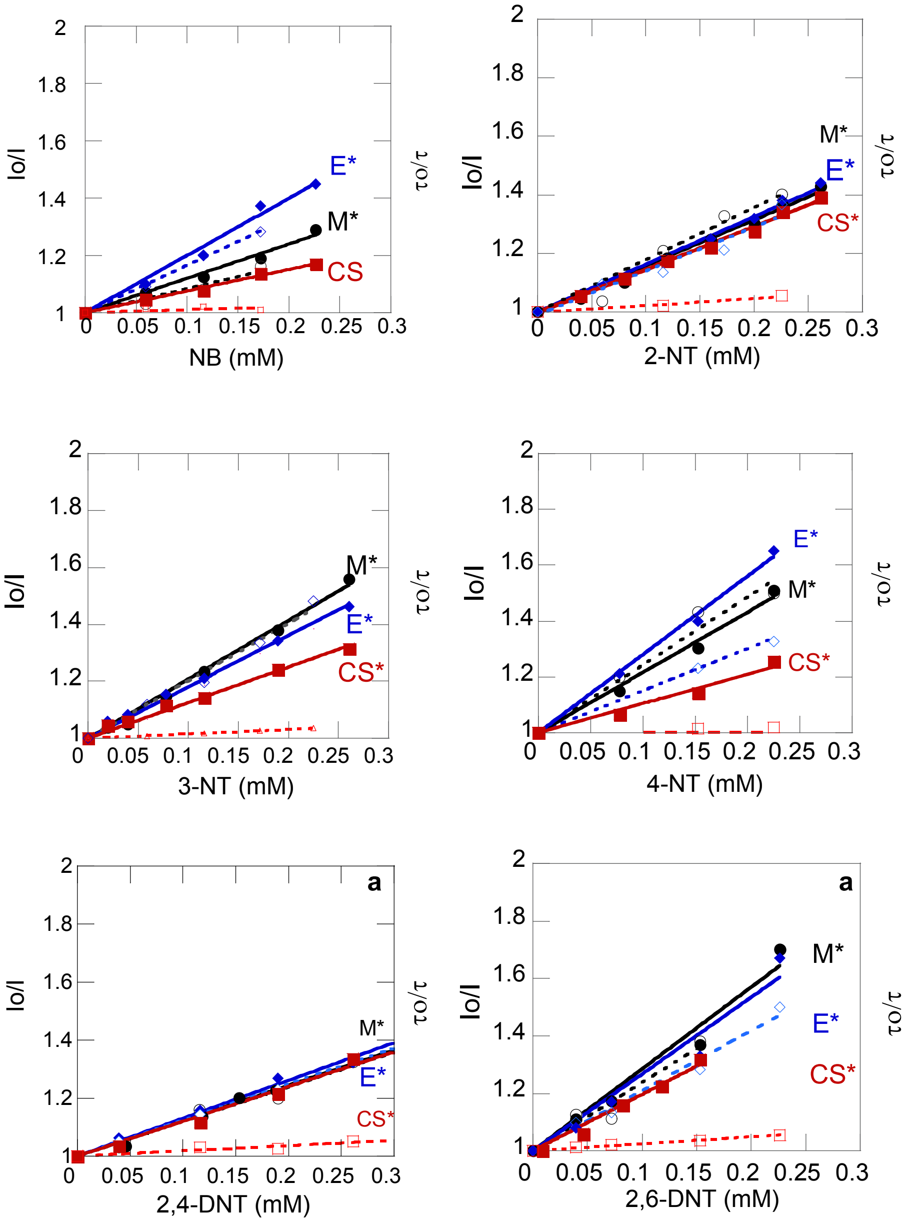


Figure S5. Stern-Volmer plots showing the intensity (▬), and lifetime (----) dependence of M*, E*, and CS* emission of CS@Py (5 nM in THF, λexc = 340 nm) on NAC concentration.

Table S2 Dynamic quenching constants of pyrene monomer, M*, pyrene excimer, E*, and nanoparticle excited state (CS*) in the CS@Py hybrid, by the nitroaromatic compounds.

	K_d		
	M*	E*	CS*
NB	838 ± 83 (0.990)	1654 ± 30 (0.998)	[b]
2NT	1780 ± 117 (0.980)	1440 ± 103 (0.980)	238 ± 32 (0.990)
3NT	2014 ± 74 (0.992)	1676 ± 58 (0.993)	157 ± 3 (0.996)
4NT	2431 ± 160 (0.988)	1509 ± 72 (0.990)	194 ± 10 (0.990)
2,4 DNT	1193 ± 58 (0.980)	1243 ± 15 (0.998)	182 ± 21 (0.990)
2,6 DNT	2374 ± 230 (0.980)	2090 ± 88 (0.992)	244 ± 9 (0.992)
TNT	2094 ± 101 (0.990)	2208 ± 108 (0.985)	456 ± 10 (0.998)

[a] K_d, (M^{-1}); data obtained from the time-resolved studies. Measurements.[b] Too small to be determined

Table S3. Quantification of TNT in TNT/NB/2,4DNT ternary mixtures

	Calculated concentration (mM)					
	C_{TNT}/C_{NB}/ $C_{2,4DNT}$ 1:0.5:0.5 molar ratio [a]			**C_{TNT}/C_{NB}/ $C_{2,4DNT}$** 1:1:1 molar ratio [b]		
	C_{TNT} (E %)[c]	**C_{NB} (E %)**	**$C_{2,4DNT}$ (E %)**	**C_{TNT} (E %)**	**C_{NB} (E %)**	**$C_{2,4DNT}$ (E %)**
M*	0.151 (2.3)	0.081 (9.5)	0.080 (8.6)	0.168 (11.2)	0.183 (23.1)	0.180 (21.0)
E*	0.152 (2.9)	0.081 (8.5)	0.082 (10.7)	0.175 (15.6)	0.186 (24.5)	0.193 (29.5)
CS*	0.141 (4.9)	0.068 (8.4)	0.070 (5.7)	0.152 (6.3)	0.173 (16.1)	0.164 (10.3)

[a] Theoretical concentration: 0.148 mM (TNT) and 0.074 mM (NB and 2,4DNT).
[b] Theoretical concentration: 0.151 mM (TNT) and 0.149 mM (NB and 2,4DNT).
[c] The E% is the ratio of the absolute error of the measurement (i.e., the difference between measured value and the actual value) to the actual value multiply by 100