Electronic Supplementary Information

Novel turn-on fluorescent sensor for cyanide ion based on the charge transfer transition of phenothiazine/indolium compounds †

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Isolation and spectral data of (*E*)-1,3,3-trimethyl-2-(2-(10-octyl-10*H*-phenothiazin-3-yl)vinyl)indoline-2-carbonitrile (PICN)

The resulting solution of the NMR titration study **PI (**10 mg, 1.6 □mol) in $CDCl_3$ and KCN (190.5 mg, 0.632 mmol) in D_2O (5.5 mL) was extracted with ethyl acetate. The combined organic layer was dried over sodium sulfate and concentrated *in vacuo*.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.1 Hz, 1H), 8.07 (d, *J* = 15.8 Hz, 1H), 7.73 – 7.42 (m, 6H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 6.4 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.38 (s, 3H), 3.89 (t, *J* = 6.7 Hz, 2H), 1.81 (s, 8H), 1.53 – 1.06 (m, 12H), 0.86 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.02, 153.45, 151.02, 142.57, 142.44, 141.61, 132.95, 130.03, 129.56, 129.14, 128.14, 127.67, 127.46, 124.37, 124.01, 123.17, 122.47, 116.23, 115.78, 114.15, 109.57, 51.90, 48.36, 36.88, 31.71, 29.20, 29.15, 27.22, 26.84, 26.77, 22.61, 14.10. IR (KBr, cm^{-1}) 2172 cm^{-1}, HRMS (ESI, positive mode, m/z): Calcd. for $[M+H]^+$ 522.2943, found 522.2927, (ESI, negative mode, m/z): Calcd. for $[M-H]^+$ 520.2786, found 520.2780.

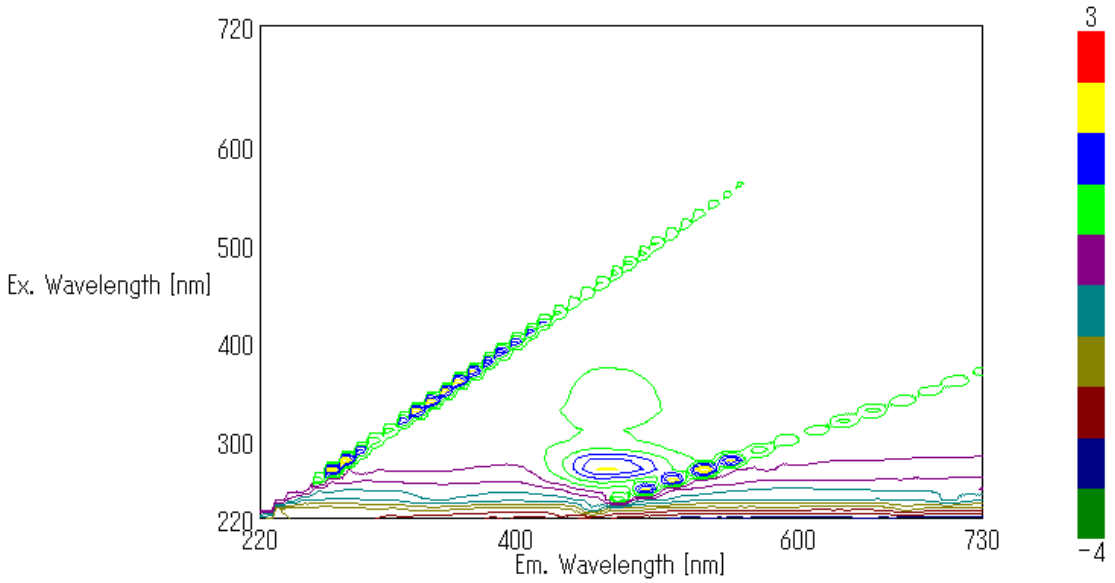

Fig. S1 The maximum search of the fluorescence obtained when adding CN^- to 2-(2-(10-hexyl-10*H*-phenothiazin-3-yl)vinyl)-1,3,3-trimethyl-3*H*-indol-1-ium iodide in the ethanol solution.

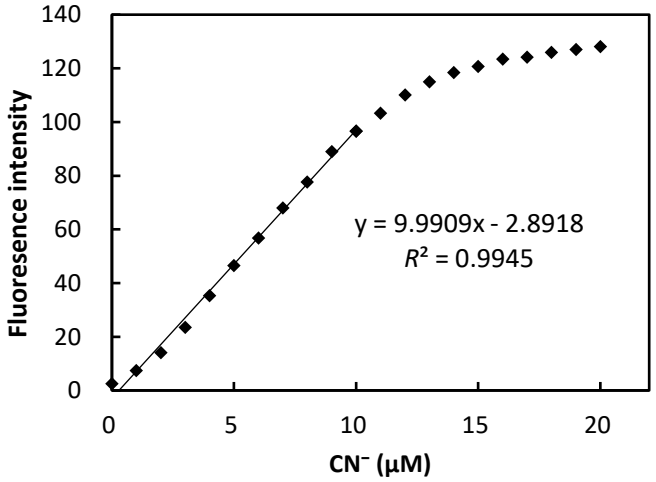

Fig. S2 Variation of the fluorescence intensity emitted at 270 nm (ex)/ 483 nm (em) for various concentrations of CN^-.

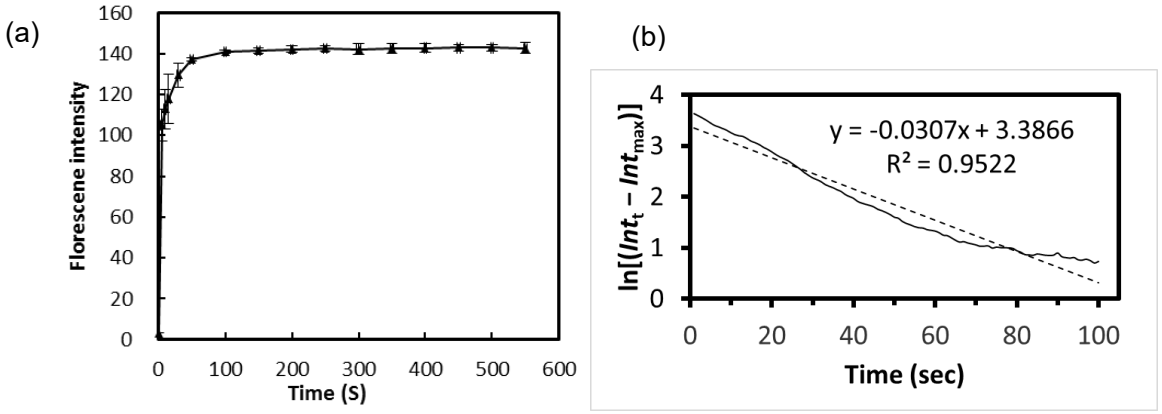

Fig. S3 (a) Change over time in the fluorescence intensity at 270 nm (ex)/ 483 nm (em) of 2-(2-(10-hexyl-10*H*-phenothiazin-3-yl)vinyl)-1,3,3-trimethyl-3*H*-indol-1-ium iodide (**PI**) (10 μM) in the presence of 20 μM CN^-. (b) Pseudo-first-order kinetic plot of the reaction between **PI** and 20 μM CN^-.

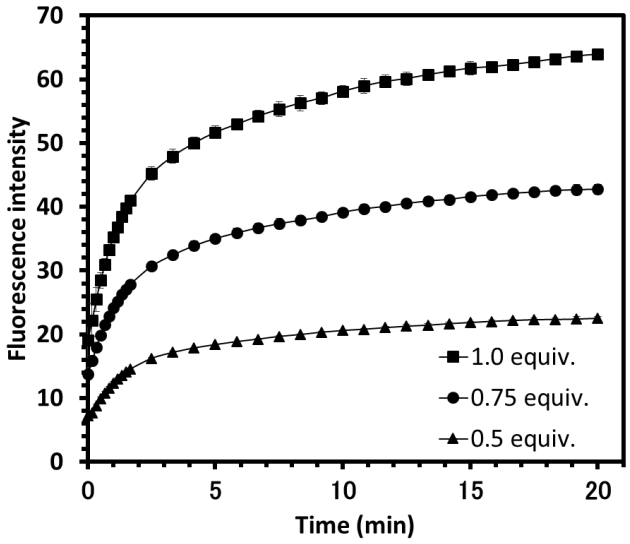

Fig. S4 Change over time in the fluorescence intensity at 270 nm (ex)/483 nm (em) of 2-(2-(10-hexyl-10*H*-phenothiazin-3-yl)vinyl)-1,3,3-trimethyl-3*H*-indol-1-ium iodide (10 μM) in the presence of 1, 0.75, and 0.5 equiv CN^-.

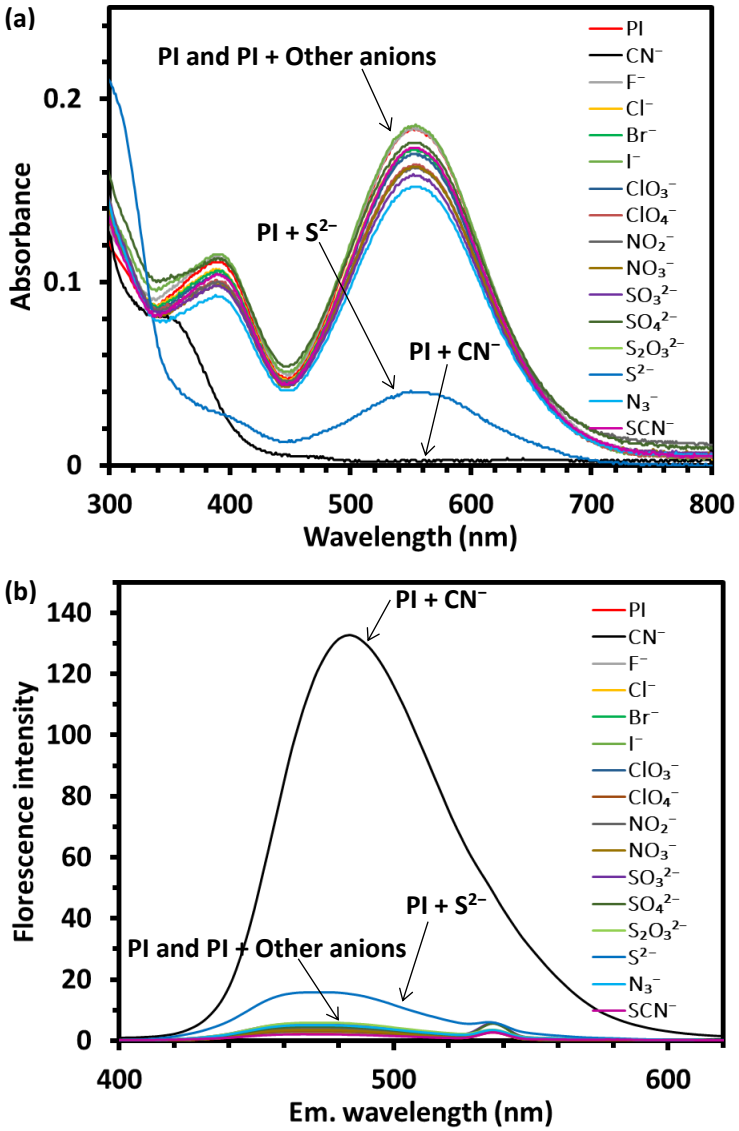

Fig. S5 (a) Absorption and (b) fluorescence spectra of 2-(2-(10-hexyl-10*H*-phenothiazin-3-yl)vinyl)-1,3,3-trimethyl-3*H*-indol-1-ium iodide (**PI**) when adding 2 equiv of different anions.

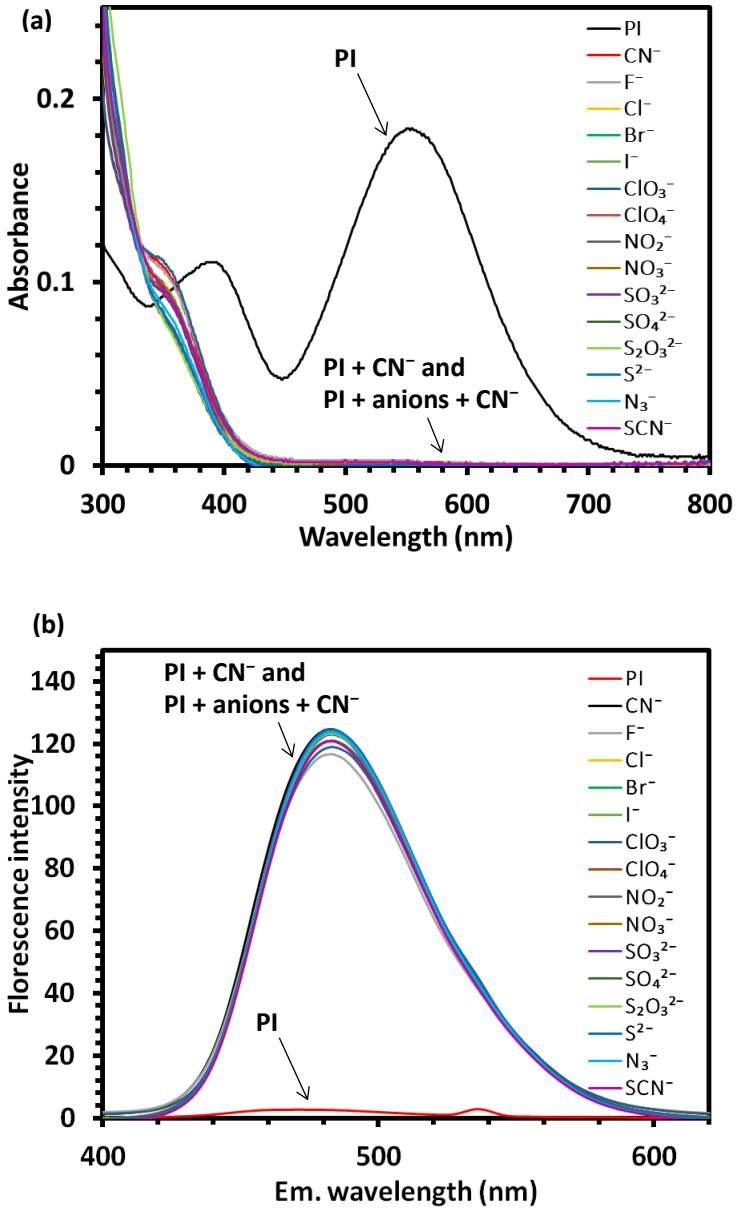

Fig. S6 (a) Absorption and (b) fluorescence spectra of 2-(2-(10-hexyl-10*H*-phenothiazin-3-yl)vinyl)-1,3,3-trimethyl-3*H*-indol-1-ium iodide (**PI**) when adding 2 equiv of different anions and 2 equiv of CN^-.

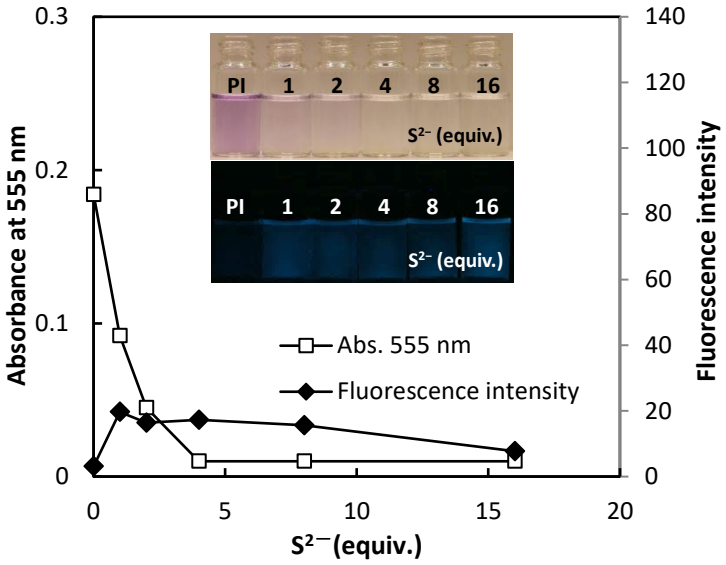

Fig. S7 Changes in the absorbance and fluorescence intensities at 483 nm of 2-(2-(10-hexyl-10*H*-phenothiazin-3-yl)vinyl)-1,3,3-trimethyl-3*H*-indol-1-ium iodide (**PI**) under an excitation wavelength of 270 nm when adding 1–16 equiv S^{2-}; the inset shows the corresponding color and fluorescence changes.

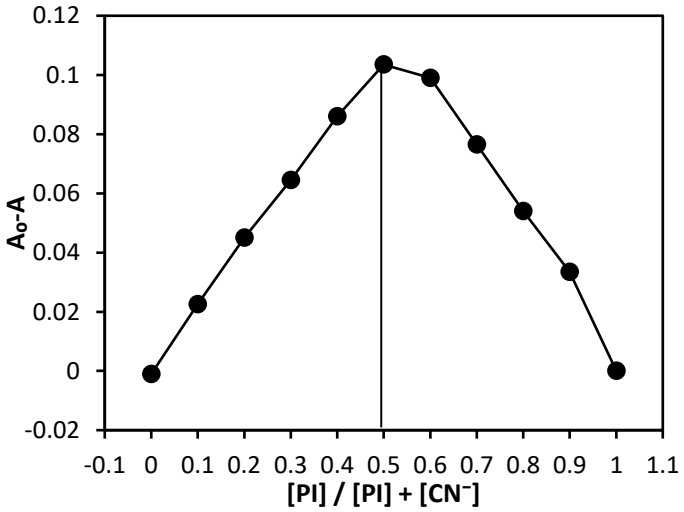

Fig. S8 Job's plot for the analysis of the reaction ratio between 2-(2-(10-hexyl-10*H*-phenothiazin-3-yl)vinyl)-1,3,3-trimethyl-3*H*-indol-1-ium iodide (**PI**) and CN^-.

Table S1. LOD of fluorometric sensor for CN containin indolium or phenothiazine moiety.

Sensor	Sensing method	LOD (nM)	References
Phenothiazine-3-dicyanovinylindan-1-one	Fluorometric	11	30
Phenothiazine-dimalononitrile	Fluorometric	3.2	31
Triphenylamine-indolium	Fluorometric	9.28	33
N-Phenyldibenzylamine-indolium	Fluorometric	0.61	33
Carbazole-heptamethine cyanine dyad	Fluorometric	9.1	35
Ethylcarbazole-benzothiazolium	Fluorometric	230	38
Coumarin-indolium	Fluorometric	444	43
Fetraphenylethylene-indolium	Fluorometric	91	44
Phenothiazine-indolium	Fluorometric	**20**	**This work**

Table S2. Parameters used to calculate the fluorescence quantum yield (Φ) (PICN: (*E*)-1,3,3-trimethyl-2-(2-(10-octyl-10*H*-phenothiazin-3-yl)vinyl)indoline-2-carbonitrile; A: absorbance at the excitation wavelength; F: integrated area under the corrected emission spectrum; η: refractive index of the solution).

Solution	Φ	A	F	η
PICN/EtOH (x)	Φ_x	0.080307	450.383	1.3618
Quinine/0.1 M H_2SO_4	0.55	0.24066	1283.84	1.3344