Supporting Information

for

Dual Optical Responses of Phenothiazine Derivatives: Near-IR Chromophore and Water-soluble Fluorescent Organic Nanoparticles

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1. General procedure for the synthesis of phenothiazine derivatives (Scheme 2).

1. 3-((E)-(4-aminostyryl))-10H-phenothiazine (**PTZ-NH**)
2. 3-((E)-(4-methoxystyryl)-10H-phenothiazine (**PTZ-OMe**)
3. 3-((E)-(4-acetoxystyryl))-10H-phenothiazine (**3**)
4. 3-((E)-2-(phenol-4-yl) vinyl)-10H-phenothiazine (**PTZ-OH**)
5. 3-((E)-2-(phenol-4-yl) vinyl)-10-methyl-phenothiazine (**MPTZ-OH**)

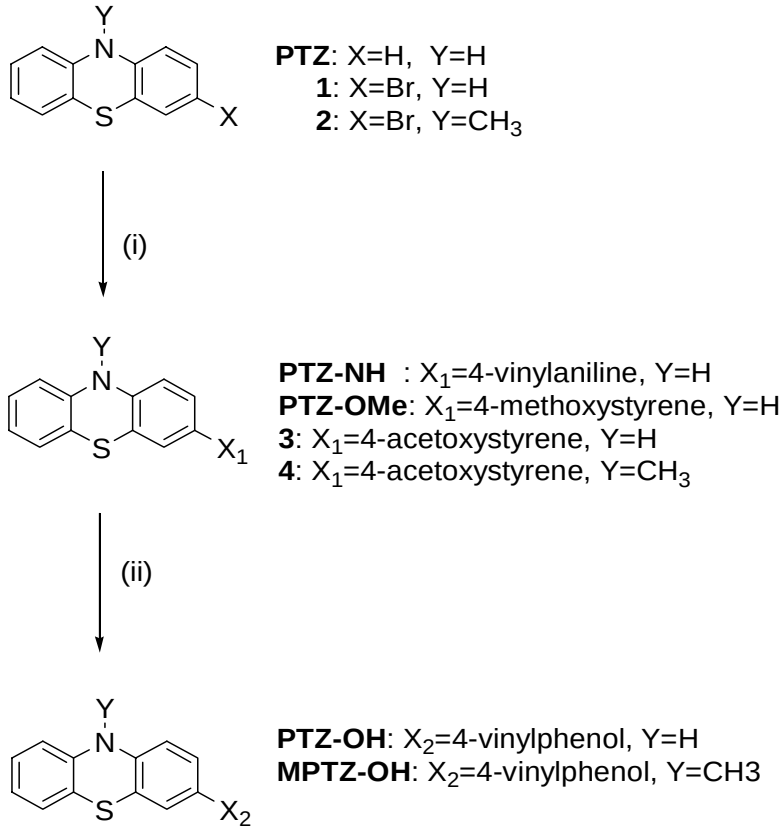
2. Figure S1 Deprotonated titration spectrum of PTZ-OH in Na_3PO_4 containing DMSO solution. Insert shows the first stage for the appearance of phenolate-PTZ, while the second stage shows the unparent appearance of phenothiazinated-PTZ and dominate component hybrid-PTZ.

3. Figure. S2 Absorption (left) and emission (right) spectral illustrations of 25 uM MPTZ-OH in alkaline aqueous solutions (10 mM). Insert photo shows the emission images under the UV light (365 nm)

4. Figure. S3 Absorption (left) and emission (right) spectral illustrations of variable concentration of PTZ-OH in KOH aqueous solutions (10 mM). Insert shows the emission intensities (at $\lambda_{500\ nm}$) plots.

1. General procedure for the synthesis of phenothiazine derivatives (Scheme 2)

Synthesis of the phenothiazine derivatives is shown in Scheme 1. 10*H*-phenothiazine or N-methyl-phenothiazine containing solution was subjected to bromination with NBS/THF in an additional funnel. Next, the samples were subjected to the Heck coupling reaction[34] with 4-vinylaniline, 4-acetoxystyrene or 4-methoxystyrene under catalyst Pd $(OAc)_2$. Finally, 4-vinylphenol substituted PTZ derivatives were easily prepared by the addition of KOH in a methanol system.



Scheme 2 Synthesis of PTZ derivatives. Reaction reagents and conditions: (i) Mixture of $Pd(OAc)_2$/$(o\text{-tol})_3P$ complex and 4-vinylaniline (for PTZ-NH) or 4-methoxyly styrene (for PTZ-OMe) or 4-acetoxyly styrene (for compound 3 and 4) with Et_3N/MeCN as a solvent pair. Reflux under nitrogen, 48 h. (ii) KOH, methanol, reflux, 4 h

1. 3-((E)-(4-aminostyryl))-10*H*-phenothiazine (PTZ-NH)

Compound 1 (5 mmole) was added to a high pressure bottle containing a mixture of palladium (II) acetate (8 mg, Strem) and tri-*o*-tolyl phosphine (80 mg, Aldrich), after which the solvent pair (triethylamine 5 mL/acetonitrile 15 mL) and 4-vinylanile (8 mmole, Acros) was added. The bottle was then sealed after bubbling with nitrogen for 10 min. After keeping the system under ~105℃ for two days, the system was cooled to room temperature and then extracted with CH_2Cl_2/H_2O twice. The organic layer was then dried with $MgSO_4$ and evaporated in under vacuum, after which the residue was subjected to chromatography on a silica gel using hexane/ethyl acetate (1/2, Rf = 0.4). A

dark-yellow solid compound was then obtained by recrystallization with acetone/hexane (yield: 52%). Data for *PTZ-NH*: ^{1}HNMR (400 Hz, DMSO-d6): δ = 8.614 (s, 1H), 7.198 (d, *J* = 8.4 Hz, 2H), 7.102 (d, *J* = 8.0 Hz, 1H), 7.052(s, 1H), 6.965 (t, *J* = 8.4 Hz, 1H), 6.898 (d, *J* =8.0 Hz, 1H), 6.840 (d, *J* =16.0 Hz, 1H), 6.728 (t, *J* =8.0 Hz, 1H), 6.690 (d, *J* =16.0 Hz, 1H), 6.650 (d, *J* = 8.0 Hz, 1H), 6.625 (d, *J* = 8.0 Hz, 1H), 6.520 (d, *J* = 8.4 Hz, 2H), 5.285 (b, 2H). Anal. Calcd. %. For $C_{20}H_{16}N_2S$: C, 75.92; H, 5.10; N, 8.85. $C_{20}H_{18}N_2OS{\cdot}1H_2O$: C, 71.83; H, 5.42; N, 8.38. Observation: C, 71.02; H, 5.49; N, 8.29.

2. 3-((E)-(4-methoxystyryl)-10*H*-phenothiazine (PTZ-OMe)

A procedure similar to that used to prepare the **PTZ-NH** was employed; however, 4-methoxystyrene (10 mmole, Merck) was added. The residue was then chromatographed on silica gel with hexane/acetone (2/1) and recrystallized from acetone/ethyl acetate (yield: 75%) to give a light-yellow solid. Data for **PTZ-OMe**: ^{1}HNMR (400 Hz, DMSO-d6): δ = 8.664 (s, 1H), 7.450 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.124 (s, 1H), 6.980 (d, *J* = 8.0 Hz, 1H), 6.938 (d, *J* = 16.2, 1H), 6.907 (d, *J* = 8 Hz, 2H), 6.879 (d, *J* = 16.2 Hz, 1H), 6.747 (t, *J* = 7.8 Hz, 1H), 6.358 (d, d = 7.8 Hz, 1H), 6.637 (d, *J* = 7.8 Hz, 2H), 3.751(s, 3H). Anal. Calcd. %. For $C_{21}H_{17}NOS$: C, 76.10; H, 5.17; N, 4.23. Observation: C, 76.01; H, 5.19; N, 4.25.

3. 3-((E)-(4-acetoxystyryl))-10*H*-phenothiazine (3)

Compound **1** (5 mmole) was added to a high pressure bottle containing a mixture of palladium (II) acetate (8 mg, Strem) and tri-*o*-tolyl phosphine (80 mg, Aldrich), after which the solvent pair (triethylamine 5 mL/acetonitrile 15 mL) and 4-acetoxystyrene (8 mmole, Merck) was added. The bottle was then sealed after bubbling with nitrogen for 10 min. After keeping the system under ~105℃ for two days, the system was cooled to room temperature and then extracted with CH_2Cl_2/H_2O twice. The organic layer was then dried using $MgSO_4$ and evaporated under vacuum, after which the residue was chromatographed on silica gel with hexane/acetone (2/1). A light yellow solid compound was obtained by recrystallization with acetone/ethyl acetate (yield: 57%). Data for **3**: ^{1}HNMR (400 Hz, DMSO-d6): δ = 8.719 (s, 1H), 7.540 (d, *J* = 8.4 Hz, 2H), 7.183 (d, *J* = 8.0 Hz, 1H), 8.163 (s, 1H), 7.090 (d, *J* = 8.4 Hz, 2H), 7.030 (s, 2H, double bond), 6.974 (t, *J* = 8.0 Hz, 1H), 6.907 (d, *J* = 8.0 Hz, 1H), 6.741 (t, *J* = 8.0 Hz, 1H), 6.663 (d, *J* = 8.0 Hz, 1H), 6.649 (d, *J* = 8.0 Hz, 1H), 2.257 (s, 3H).

4. 3-((E)-2-(phenol-4-yl)vinyl)-10*H*-phenothiazine (PTZ-OH)

After refluxing compound **3** with excess KOH in methanol for four hours, the system was evaporated in vacuum and the sample was then extracted with CH_2Cl_2/1N HCl twice. Next, the organic layer was dried with $MgSO_4$ and the collected residue was chromatographed on a silica gel using hexane/acetone (1/2). Finally, yellow powders (yield: 92%) were recrystallized with

acetone/hexane. Data for **PTZ-OH**: ^{1}H NMR (DMSO-d6): δ = 9.497 (s, 1H), 8.650 (s, 1H), 7.332 (d, *J* = 8.4 Hz, 2H), 7.137 (d, *J* = 8.0 Hz, 1H), 7.098 (s, 1H), 6.970 (t, *J* = 8.0 Hz, 1H), 6.925 (d, *J* = 16.4 Hz, 1H), 6.903 (d, *J* = 8.0 Hz, 1H), 6.801 (d, *J* = 16.4 Hz, 1H), 6.735 (t, *J* = 8.0 Hz, 1H), 6.725 (d, *J* = 8.4 Hz,2H), 6.656 (d, *J* = 8.0 Hz, 1H), 6.628 (d, *J* = 8.0 Hz, 1H). Anal. Calcd. %. For $C_{25}H_{15}NOS$: C, 75.68; H, 4.76; N, 4.41. Observation: C, 75.58; H, 4.79; N, 4.40.

5. 3-((E)-2-(phenol-4-yl) vinyl)-10-methyl-phenothiazine (MPTZ-OH)

Compound *3-((E)-(4-acetoxystyryl))-10-methyl-phenothiazine (**4**)***,*** the precursor of **MPTZ-OH,** was prepared following the same procedure used to prepare compound **3**, except that compound **2** was used as the starting material. The residue was then chromatographed on silica gel by hexane/acetone (3/1, Rf = 0.5). A light-yellow solid was collected by recrystallization with methanol (yield: 65%). Data for **4**: ^{1}H NMR (DMSO-d6): δ = 7.570 (d, *J* = 8.4 Hz, 2H), 7.413 (s, 1H), 7.304 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.206 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.166 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.150 (d, *J* = 16.2 Hz, 1H), 7.123 (d, *J* = 16.2 Hz, 1H), 7.098 (d, *J* = 8.4 Hz, 2H), 6.950 (m, 3H), 3.311 (s, 3H), 2.234 (s, 3H).

Following the preparation of **PTZ-OH**, the final product was chromatographed on silica gel by hexane/acetone (3/1, Rf = 0.4) and a yellow powder was recrystallized from hexane/acetone (yield: 90 %). Data for **MPTZ-OH**: ^{1}HNMR (400 Hz, DMSO-d6): δ = 9.559 (s, 1H), 7.358 (d, *J* = 8.4 Hz, 2H), 7.339 (m, 2H), 7.198 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.147 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.018 (d, *J* = 16.0 Hz, 1H), 6.940 (m, 2H), 6.904 (d, *J* = 8.0 Hz, 1H), 6.888 (d, *J* = 16.0 Hz, 1H), 6.734 (d, *J* = 8.4 Hz, 2H), 3.257 (s, 3H). Anal. Calcd. %. For $C_{21}H_{17}NOS$: C, 76.10; H, 5.17; N, 4.23. Observation: C, 75.69; H, 5.20; N, 4.20.

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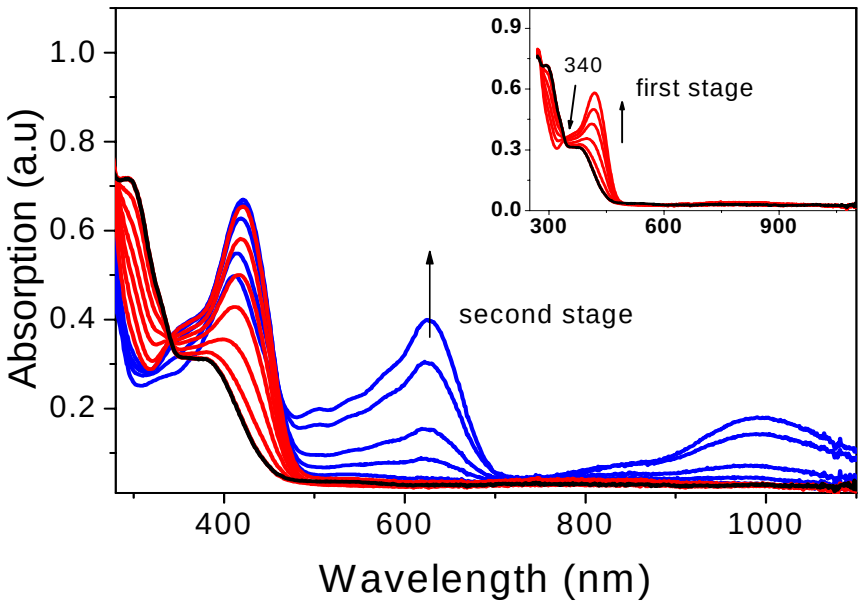

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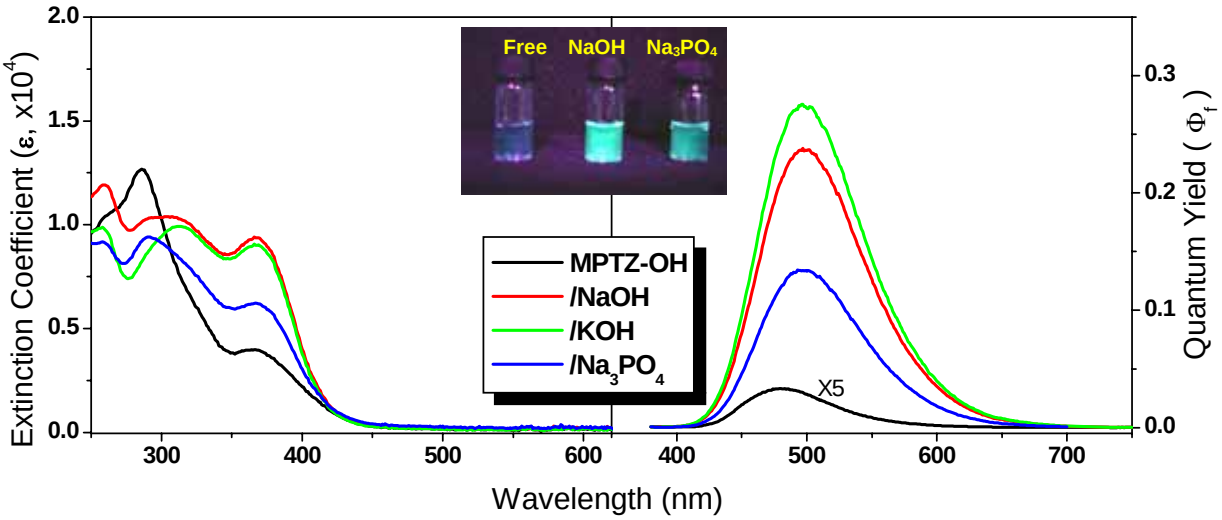

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