Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Enhanced Photocatalytic Hydrogen Production by Introducing Carboxylic Acid Group into Cobaloxime Catalysts

Junfei Wang,[a b] Chao Li,[a] Qianxiong Zhou,[a] Weibo Wang,[a] Yuanjun Hou,*[a] Baowen Zhang,[a] Xuesong Wang*[a]

[a] Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

[b] Graduate School of Chinese Academy of Sciences, Beijing 100049, P. R. China

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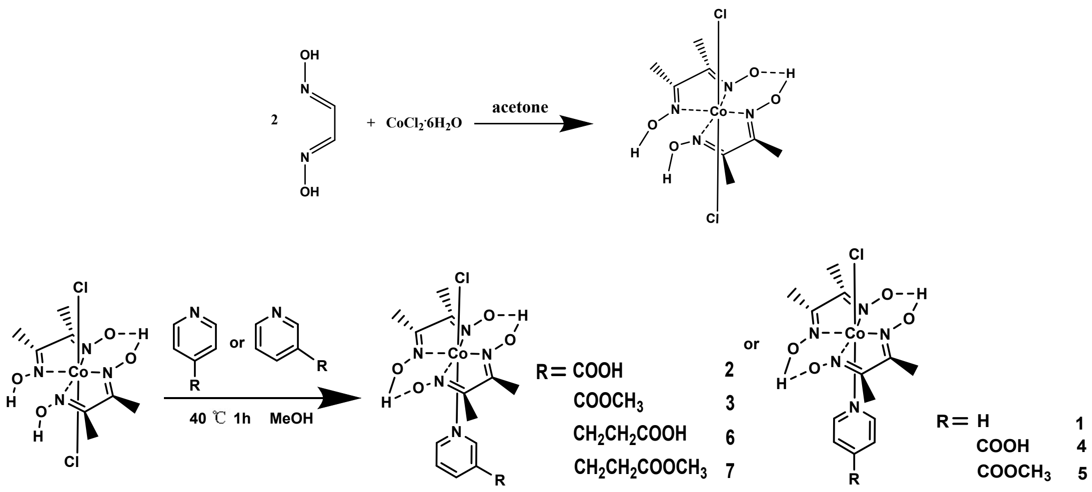
Synthesis and characterization



Scheme S1. Synthetic routes for **1-7**.

Synthesis of [CoCl$_2$(dmgH)(dmgH$_2$)].[1] CoCl$_2$.6H$_2$O (50 g, 0.210 mol) was dissolved in acetone (1.5 L) and dimethylglyoxime (49 g, 0.422 mol) was added. The mixture was agitated for 10 min and filtered to remove any un-dissolved material. The green crystals formed when the solution was allowed to stand overnight were collected and washed with acetone. Yield, 59.5 g (79%).

Synthesis of 1-7. Et$_3$N (42 mL, 0.3 mmol) was added to a stirred suspension of [CoCl$_2$(dmgH)(dmgH$_2$)] (108 mg, 0.3 mmol) in MeOH (8 mL), resulting in a brown solution. Pyridine or its derivative was added after five minutes and the reaction mixture was heated at 40°C for one hour. The solution was allowed to cool to room temperature to precipitate the brown product, which was filtered off, washed with water (10 mL), ethanol (10 mL), and diethyl ether (10 mL) and dried under high vacuum.

Complex 1. ^{1}H NMR (400 MHz，d$_6$-DMSO)**:** δ in ppm 18.49 (br, 2O*H*), 8.03 (d, *J* = 5.2 Hz, 2H, py), 7.90 (m, 1H, py)，7.47 (m, 2H, py), 2.32 (s, 12H, dmg^{2-}). MS (ESI, CH$_3$CN): m/z = 404.0523 ([M+H]$^+$); 368.0758 ([M-Cl]$^+$); 289.0336 ([M-Cl-py]$^+$). Anal. calcd for C$_{13}$H$_{19}$N$_5$ClCoO$_4$: C, 38.68; H, 4.74; N, 17.35. Found: C, 38.77; H, 4.77; N, 17.20.

Complex 2. ^{1}H NMR (400 MHz，d$_6$-DMSO)**:** δ in ppm 18.45 (br, 2O*H*), 13.96 (s , H, 3-COO*H*), 8.61(s, H, py), 8.32 (d, *J* = 7.6 Hz, 1H, py), 8.20 (d, *J* = 5.6 Hz, 1H, py), 7.62 (m, 1H, py), 2.31 (s, 12H, dmg^{2-}). MS (ESI, CH$_3$CN): m/z = 448.0421 ([M+H]$^+$); 412.0654 ([M-Cl]$^+$); 289.0337 ([M-Cl-py-*m*-COOH]$^+$). Anal. calcd for C$_{14}$H$_{19}$N$_5$ClCoO$_6$ • 2H$_2$O: C, 34.76; H, 4.79; N, 14.48. Found: C, 34.77; H, 4.70; N, 14.26.

Complex 3. ^{1}H NMR (400 MHz，d$_6$-DMSO)**:** δ in ppm 18.50 (br, 2O*H*), 8.69 (s, H, py), 8.28 (d, *J* = 6.0 Hz, 1H, py)，8.26 (d, *J* = 1.2 Hz, 1H, py), 7.42 (m, H, py), 3.91 (s, 3H, -CH$_3$), 2.31 (s, 12H, dmg^{2-}). MS (ESI, CH$_3$CN): m/z = 462.0576 ([M+H]$^+$); 426.0810 ([M-Cl]$^+$); 289.0335 ([M-

Cl-py-*m*-$COOCH_3]^+$). Anal. calcd for $C_{15}H_{21}N_5ClCoO_6$: C, 39.02; H, 4.58; N, 15.17. Found: C, 38.77; H, 4.64; N, 14.82

Complex 4. ^1H NMR (400 MHz，d_6-DMSO)**:** δ in ppm 18.43 (br, 2O*H*), 14.04 (s , 1H, 4-COO*H*), 8.22 (d, *J* = 6.4 Hz, 2H, py), 7.86 (d, *J* = 6.4 Hz, 2H, py)，2.31 (s, 12H, dmg^{2-}). MS (ESI, CH_3CN): m/z = 448.0421 ($[M+H]^+$); 412.0654 ($[M-Cl]^+$); 289.0337 ([M-Cl-py-*p*-$COOH]^+$). Anal. calcd for $C_{14}H_{19}N_5ClCoO_6 \cdot H_2O$: C, 36.10; H, 4.54; N, 15.04. Found: C, 35.78; H, 4.55; N, 14.90.

Complex 5. ^1H NMR (400 MHz，d_6-DMSO)**:** δ in ppm 18.49 (br, 2O*H*), 8.32 (d, J = 6.8 Hz, 2H, py), 7.73 (d, J = 6.4 Hz, 2H, py)，3.87 (s, 3H, -CH_3), 2.31 (s, 12H, dmg^{2-}). MS (ESI, CH_3CN): m/z = 462.0580 ($[M+H]^+$); 426.0812 ($[M-Cl]^+$); 289.0336 ([M-Cl-py-*p*-$COOCH_3]^+$). Anal. calcd for $C_{15}H_{21}N_5ClCoO_6$: C, 39.02; H, 4.58; N, 15.17. Found: C, 39.22; H, 4.65; N, 15.02.

Complex 6. ^1H NMR (400 MHz，d_6-DMSO)**:** δ in ppm 18.43 (br, 2O*H*), 12.18 (s , H, 3-CH_3CH_2COO*H*),7.88 (d, *J* = 6.8 Hz, 2H, py), 7.80 (d, *J* = 7.6 Hz, 1H, py)，7.38 (m, 1H, py), 2.72 (t, *J* = 7.2 Hz, 2H, -CH_2-), 2.48 (d, *J* = 7.2 Hz, 2H, -CH_2-), 2.32 (s, 12H, dmg^{2-}). MS (ESI, CH_3CN): m/z = 476.0736 ($[M+H]^+$); 440.0968 ($[M-Cl]^+$); 289.0336 ([M-Cl-py-*m*-$CH_2CH_2COOH]^+$). Anal. calcd for $C_{16}H_{23}N_5ClCoO_6 \cdot 0.5H_2O$: C, 39.64; H, 4.99; N, 14.45. Found: C, 39.58; H, 5.08; N, 14.21.

Complex7. ^1H NMR (400 MHz，d_6-DMSO)**:** δ in ppm 18.44 (br, 2O*H*), 7.89 (d, *J* = 9.2 Hz, 2H, py), 7.81(d, *J* = 8.0 Hz, 1H, py)，7.39 (m, 1H, py), 3.58 (s, 3H, -CH_3), 2.76 (t, *J* = 7.2 Hz, 2H, -CH_2-), 2.58 (t, *J* = 7.2 Hz, 2H, -CH_2-), 2.32 (s, 12H, dmg^{2-}). MS (ESI, CH_3CN): m/z = 490.0891 ($[M+H]^+$); 454.1123 ($[M-Cl]^+$); 289.0335 ([M-Cl-py-*m*-$CH_2CH_2COOCH_3]^+$). Anal. calcd for $C_{17}H_{25}N_5ClCoO_6$: C, 41.69; H, 5.14; N, 14.30. Found: C, 41.36; H, 5.09; N, 14.12.

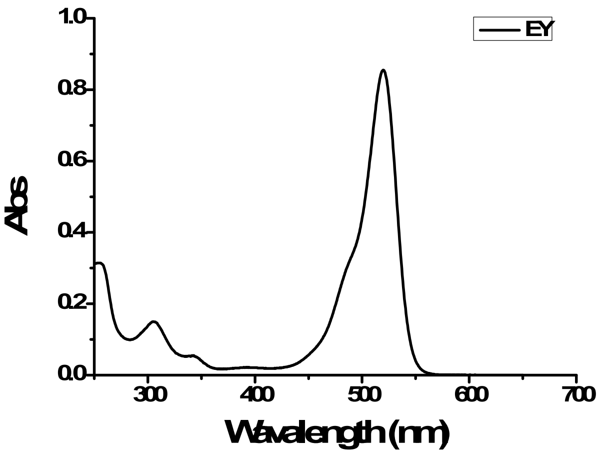


Figure S1. UV-visible absorption spectrum of Eosin Y (0.01 mM) in CH_3CN/H_2O (1:1).

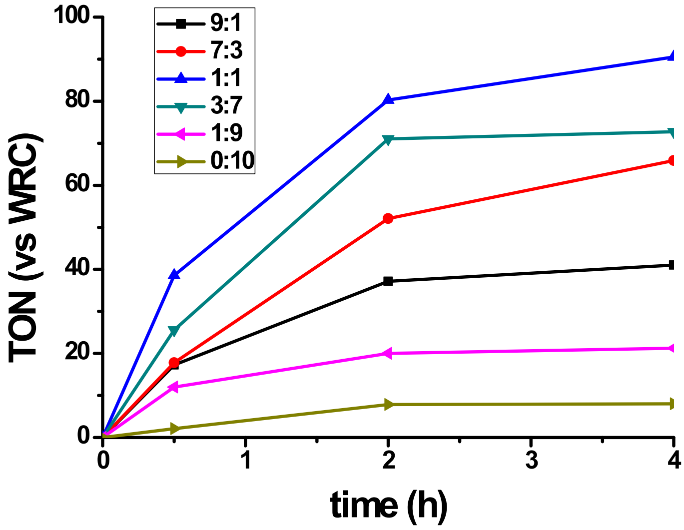


Figure S2. Photocatalytic H_2 production profiles of the AP systems containing 0.025 mM Eosin Y, 0.1 mM **6**, 4% TEOA in CH_3CN/H_2O (pH = 7.5) of varied compositions.

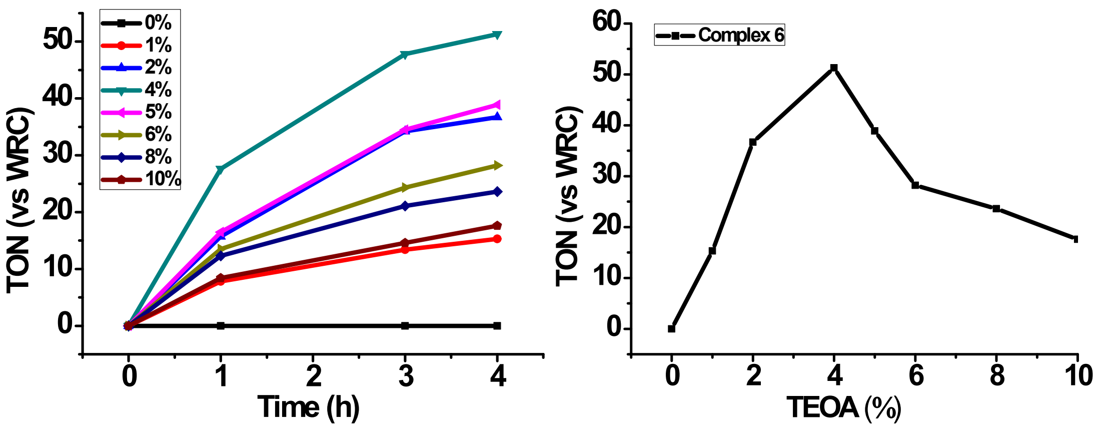


Figure S3. (a) Photocatalytic H_2 production profiles of the AP systems containing 0.025 mM Eosin Y, 0.1 mM **6**, and varied concentrations of TEOA in CH_3CN/H_2O (1:1, pH = 7.5); (b) H_2 production amounts of the AP systems after 4 h irradiation.

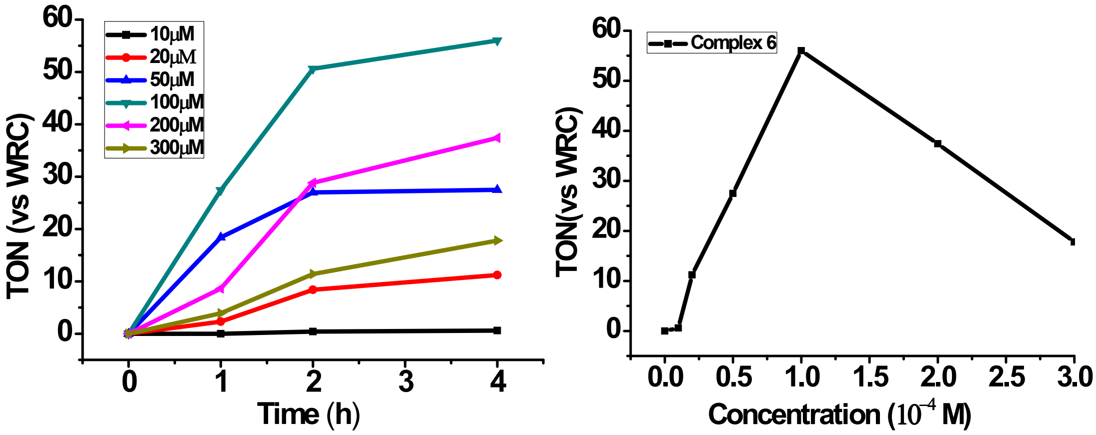


Figure S4. (a) Photocatalytic H_2 production profiles of the AP systems containing 0.025 mM Eosin Y, 4% TEOA, and varied concentrations of **6** in CH_3CN/H_2O (1:1, pH = 7.5); (b) H_2 production amounts of the AP systems after 4 h irradiation.

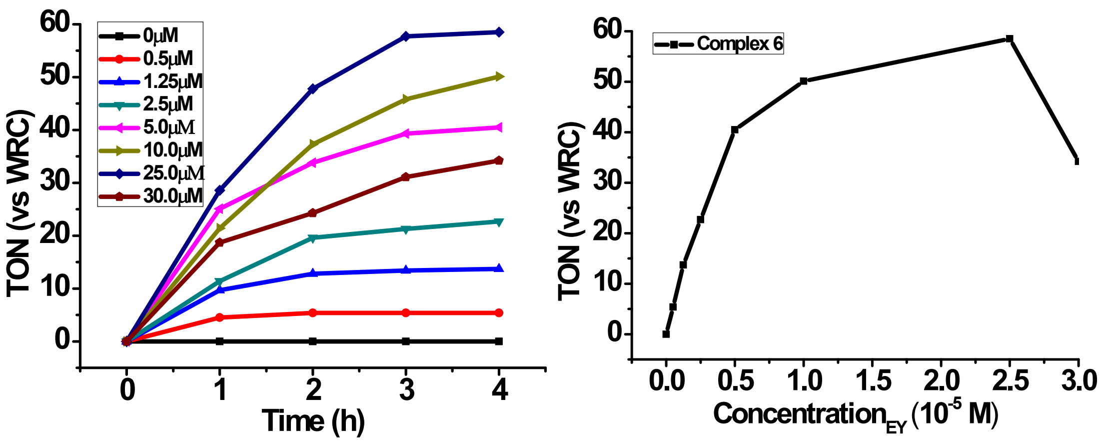


Figure S5. (a) Photocatalytic H_2 production profiles of the AP systems containing 0.1 mM **6**, 4% TEOA, and varied concentrations of Eosin Y in CH_3CN/H_2O (1:1, pH = 7.5); (b) H_2 production amounts of the AP systems after 4 h irradiation.

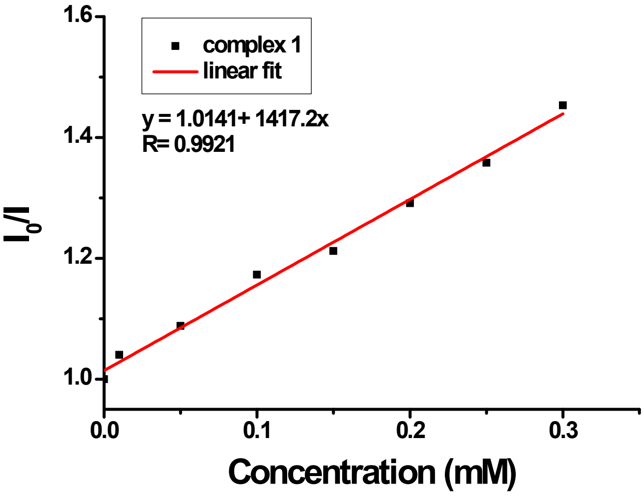


Figure S6. Stern-Volmer plot of the fluorescence quenching of Eosin Y by **1** in CH_3CN/H_2O (1:1, pH = 7.5).

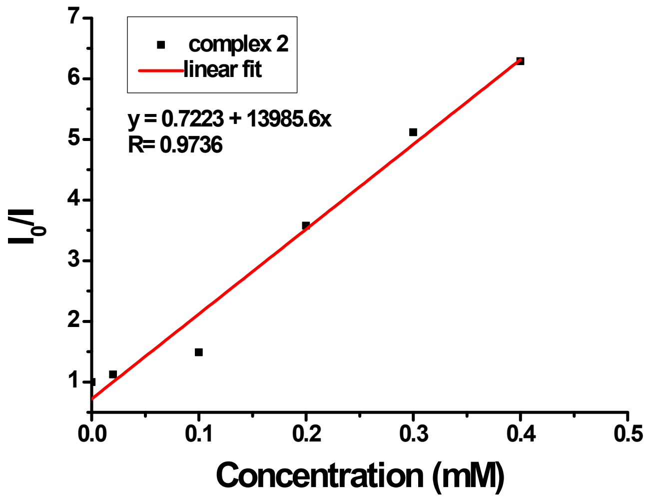


Figure S7. Stern-Volmer plot of the fluorescence quenching of Eosin Y by **2** in CH_3CN/H_2O (1:1, pH = 7.5).

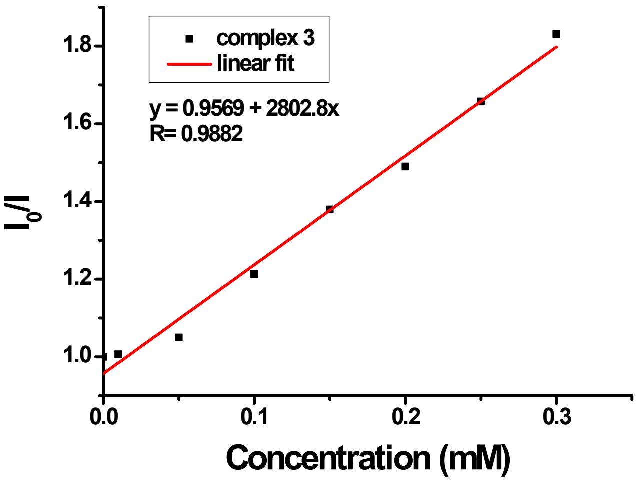


Figure S8. Stern-Volmer plot of the fluorescence quenching of Eosin Y by **3** in CH_3CN/H_2O (1:1, pH = 7.5).

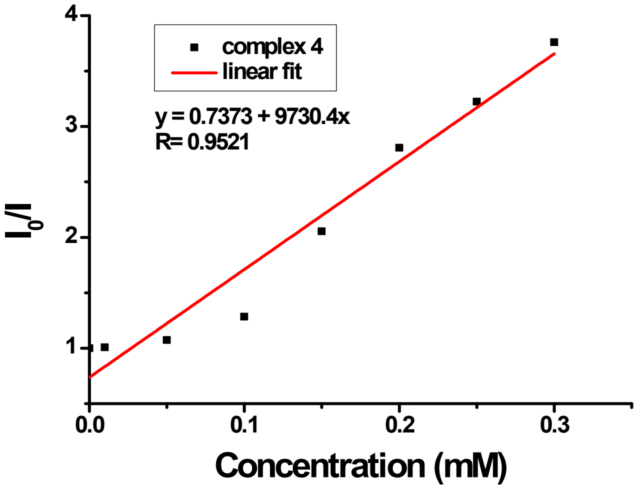


Figure S9. Stern-Volmer plot of the fluorescence quenching of Eosin Y by **4** in CH_3CN/H_2O (1:1, pH = 7.5).

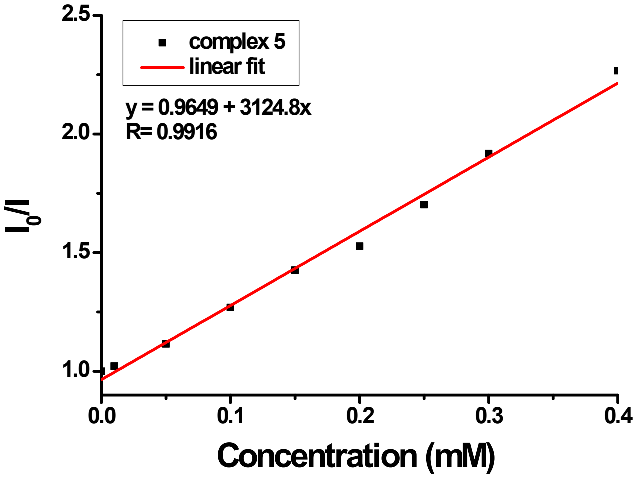


Figure S10. Stern-Volmer plot of the fluorescence quenching of Eosin Y by **5** in CH_3CN/H_2O (1:1, pH = 7.5).

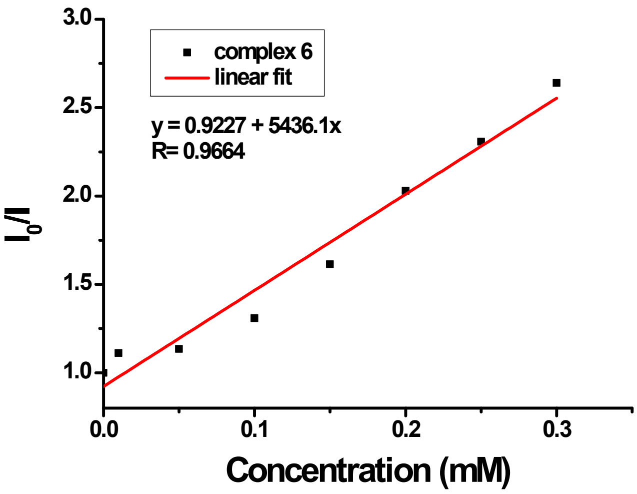


Figure S11. Stern-Volmer plot of the fluorescence quenching of Eosin Y by **6** in CH_3CN/H_2O (1:1, pH = 7.5).

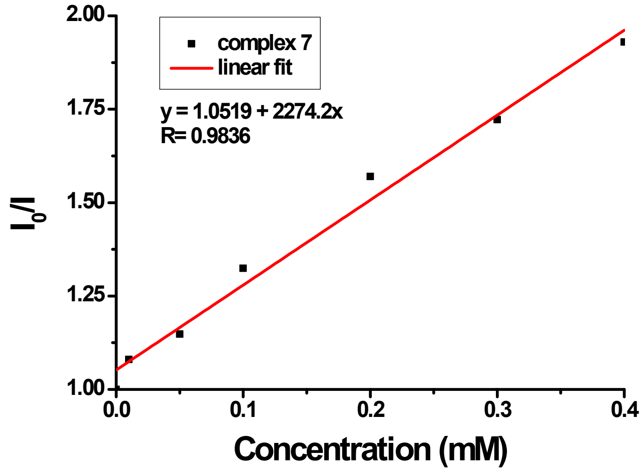


Figure S12. Stern-Volmer plot of the fluorescence quenching of Eosin Y by **7** in CH_3CN/H_2O (1:1, pH = 7.5).

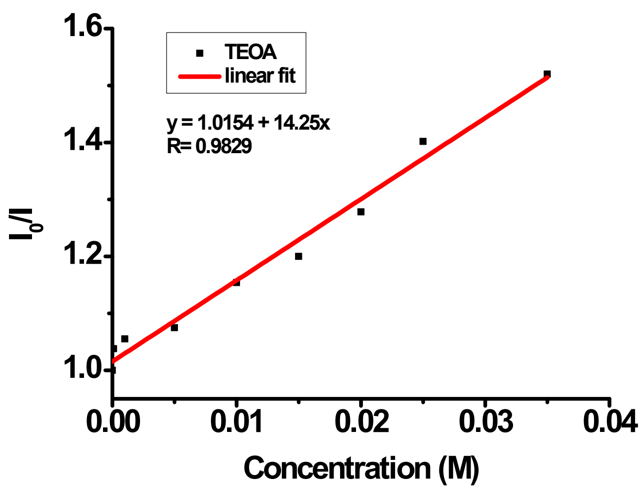


Figure S13. Stern-Volmer plot of the fluorescence quenching of Eosin Y by TEOA in CH_3CN/H_2O (1:1, pH = 7.5).

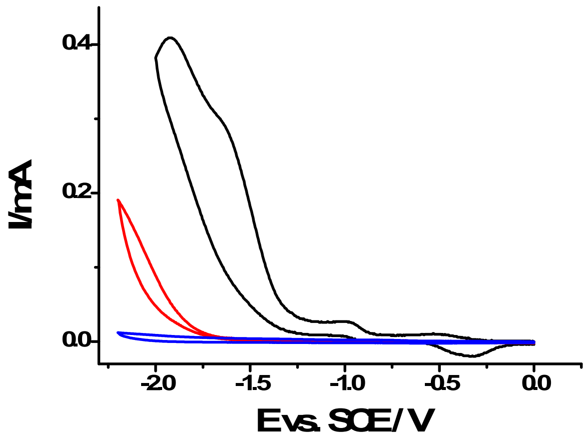


Figure S14. Cyclic voltammograms of blank CH_3CN (blue), 15 equiv acetic acid in CH_3CN (red), and 15 equiv acetic acid and 1 equiv **6** (1 mM) in CH_3CN (black).

References

1. (a) W. C. Trogler, R. C. Stewart, L. A. EPPS and L. G. Marzilli, *Inorg. Chem.*, 1974, **13**, 1564-1570.