Electronic Supplementary Information for "Colorimetric and Fluorometric Detection of Cationic Surfactants Based on Conjugated Polydiacetylene Supramolecules"

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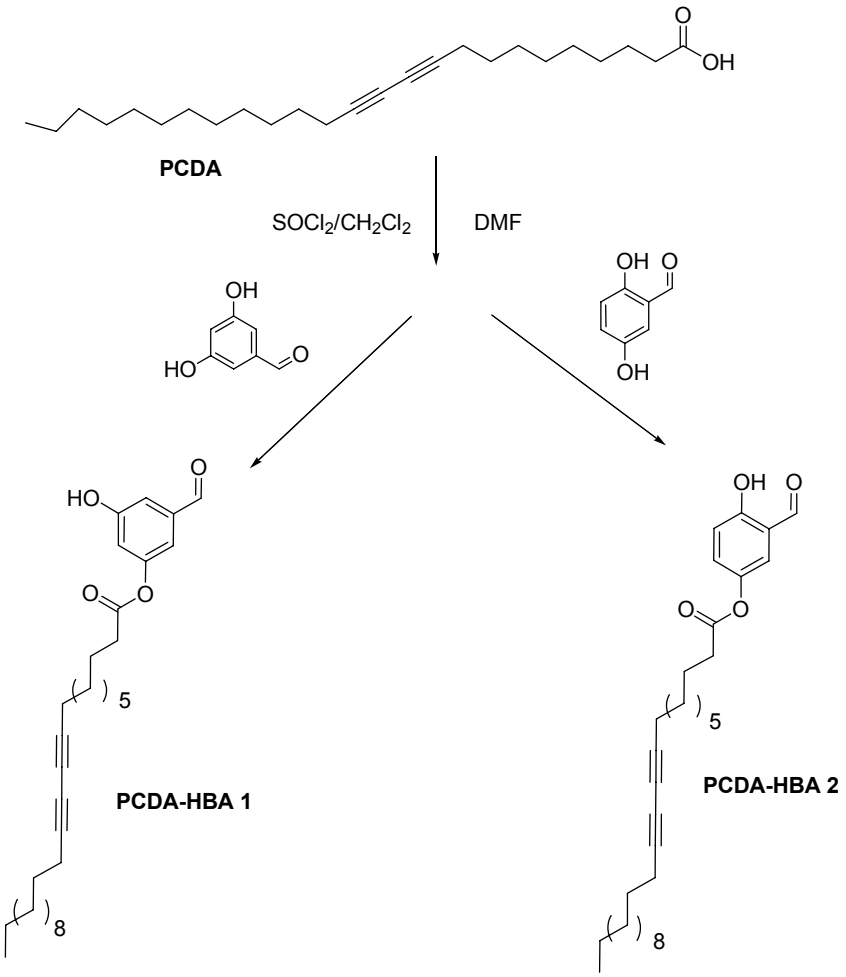
Experimental Section

General methods. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Flash chromatography was carried out on silica gel 60 (230-400 mesh ASTM; Merck). Thin layer chromatography (TLC) was carried out using Merck 60 F_{254} plates with a thickness of 0.25 mm. Preparative TLC was performed using Merck 60 F_{254} plates with a thickness of 1 mm. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker 250 or Varian 500. Mass spectra were obtained using a JMS-HX 110A/110A Tandem Mass Spectrometer (JEOL). UV absorption spectra were obtained on UVIKON 933 Double Beam UV/VIS Spectrometer. Fluorescence emission spectra were obtained using RF-5301/PC Spectrofluorophotometer (Shimadzu).

Synthesis



The diacetylene monomers **PCDA-1 and PCDA-2** were prepared from commercially available 10,12-pentacosadiynoic acid (Alfa) by coupling the acid

with corresponding phenol. A typical procedure for the preparation of **PCDA-HBA 1** is as follows. To a solution containing 0.500 g (1.34 mmol) of 10,12-pentacosadiynoic acid in 10 mL of methylene chloride was added dropwise 0.55 g (4.32 mmol) of oxalyl chloride at room temperature. The resulting solution was stirred at room temperature for 1 h. To the solution was added a catalytic amount (one drop) of DMF and stirred for additional hour. After concentrating *in vacuo*, the residue was redissolved in 10 mL of methylene chloride. The resulting solution was added dropwise to the solution containing 0.300 g (2.17 mmol) of 3,5-dihydroxybenzaldehyde in 10 mL of THF. The resuting mixture was allowed to stir for overnight at room temperature. The solvent was removed *in vacuo* and the residue was purified by silica gel column chromatography (CH_2Cl_2/CH_3OH 99:1) to give 0.354 g (53%) of the desired diacetylene monomer **PCDA-HBA 1** as a white solid. The diacetylene monomers **PCDA-HBA 2** were also prepared by employing similar procedure, and the product was purified by silica gel column chromatography (Hexane/CH_2Cl_2 33:67) to give 0.51 g (76%). Spectroscopic data for the monomers are as follows:

PCDA-HBA 1: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, 3H), 1.25-1.75 (m, 36H), 2.24 (t, 4H), 2.58 (t, 2H), 6.88 (t, 1H), 7.20-7.23 (m, 2H), 9.92 (d, 1H); ^{1}H NMR (62.5 MHz, $CDCl_3$) δ 13.103, 18.161, 21.659, 23.746, 27.233, 27.304, 27.695, 27.833, 27.952, 28.015, 28.064, 28.317, 28.447, 28.595, 30.883, 64.138, 64.278, 112.049, 114.483, 114.575, 137.242, 151.021, 156.384, 171.297, 190.205; HRMS (FAB) m/z 495.3477 ($C_{32}H_{46}O_4$ requires 495.3474).

PCDA-HBA 2: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.87 (t, 3H), 1.25-1.76 (m, 36H), 2.24 (t, 4H), 2.53 (t, 2H), 6.98-7.03 (m, 1H), 7.31-7.33 (m, 1H), 7.26-7.28b(m, 1H), 9.84-9.87 (m, 1H), 10.90-10.93 (m, 1H); ^{1}H NMR (62.5 MHz, $CDCl_3$) δ 14.141, 19.188, 22.696, 24.812, 28.257, 28.332, 28.721, 28.873, 29.010, 29.081, 29.351, 29.481, 29.634, 31.918, 34.178, 65.146, 65.305, 118.676, 120.126, 125.377, 130.766, 143.022, 159.198, 172.419, 195.815; HRMS (EI) m/z 495.3477 ($C_{32}H_{46}O_4$ requires 495.3474).

Preparation of micelle

Preparation of PDA vesicles in aqueous solution was achieved by the following method. Briefly, a diacetylene monomer was dissolved in a small amount of DMSO (1 mL), and the organic solution was injected into 9 mL HEPES buffer (20 mM, pH 7.4) while shaking the mixed solution to yield a total monomer concentration of 1 mM. The sample was then sonicated at 80 ^{o}C for 25 min. The resulting solution was filtered through a 0.8 μm filter and the filtrate was cooled at 4 ^{o}C for 12 h. Polymerization was carried out at room temperature by irradiating the solution with 254 nm UV light (1 mW/cm2).

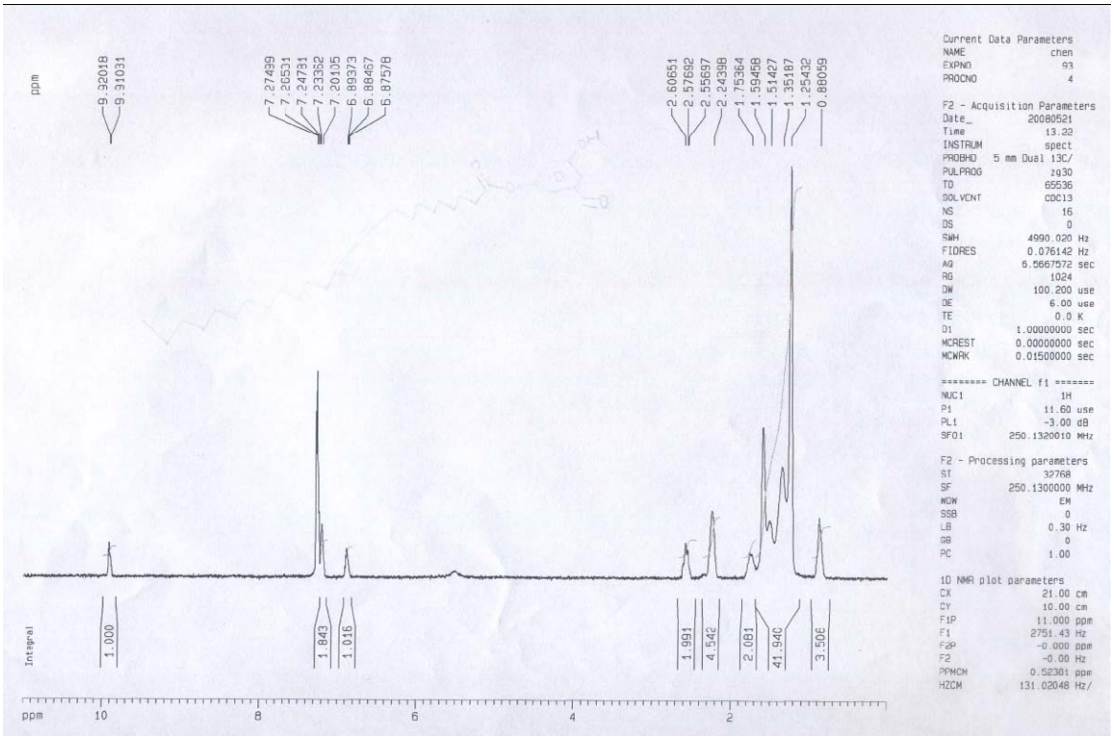


Fig. S1. ^{1}H NMR (250 MHz) of compound **PCDA-HBA 1** in $CDCl_3$.

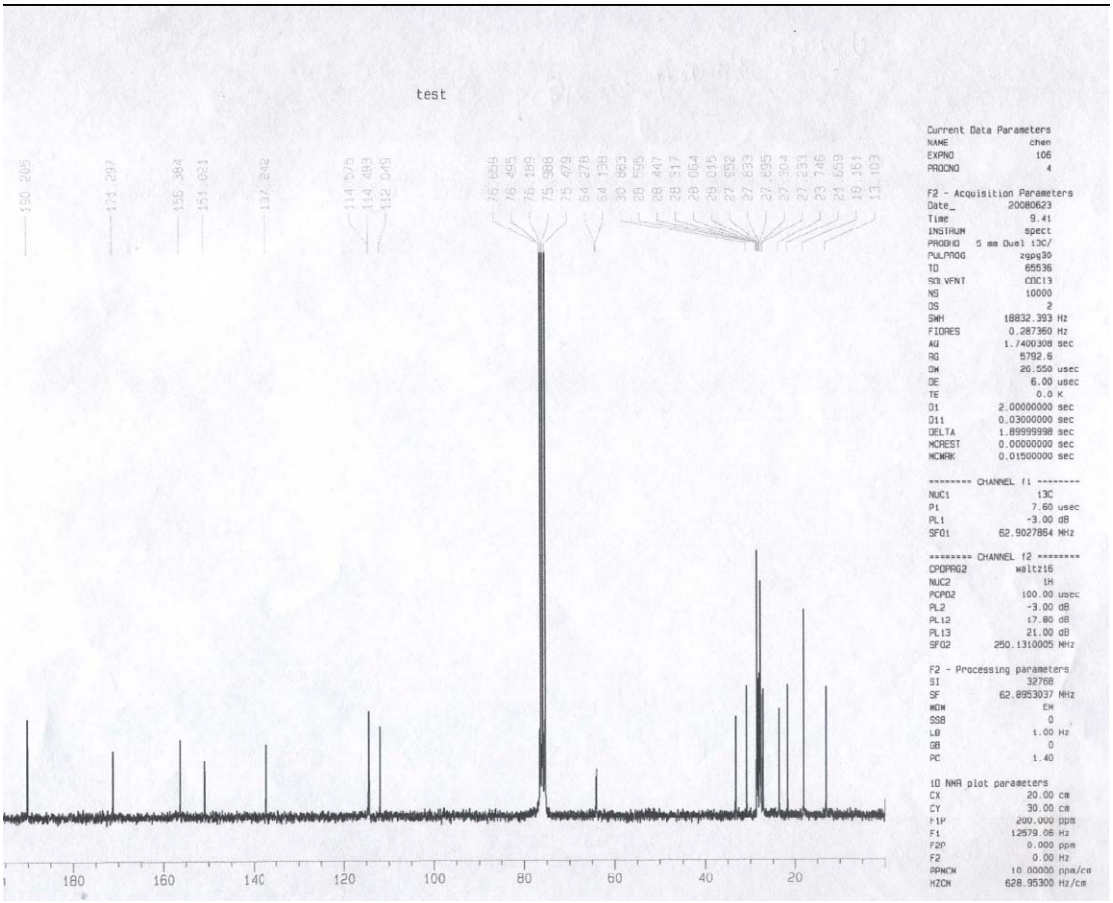


Fig. S2. ^{13}C NMR (62.5 MHz) of compound **PCDA-HBA 1** in $CDCl_3$.

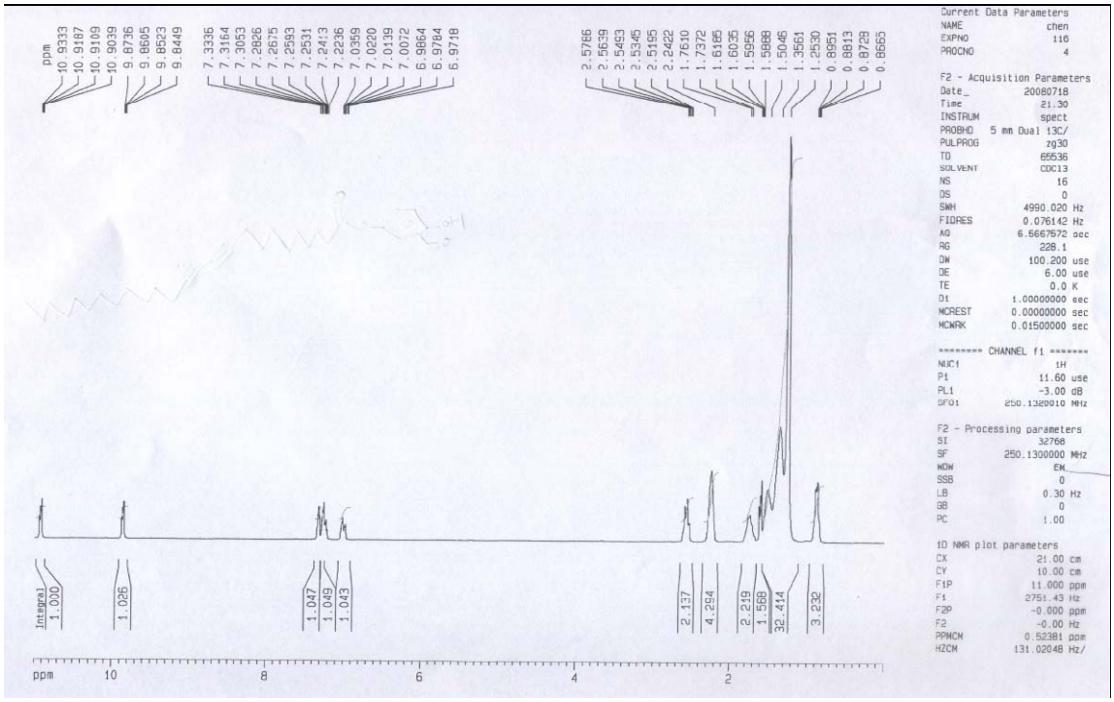


Fig. S3. ^{1}H NMR (250 MHz) of compound **PCDA-HBA 2** in $CDCl_3$.

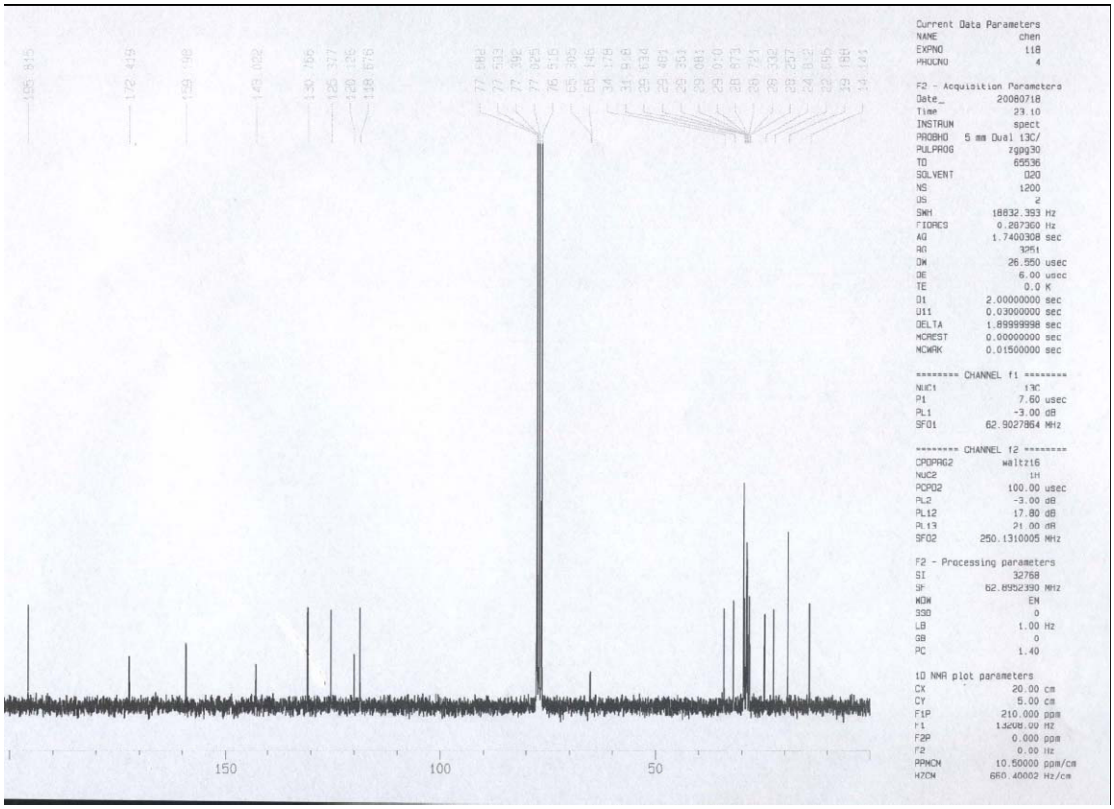


Fig. S4. ^{13}C NMR (62.5 MHz) of compound **PCDA-HBA 2** in $CDCl_3$.

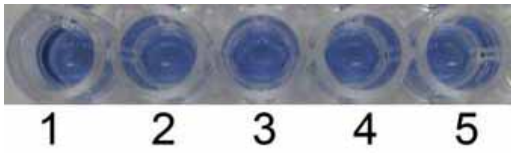


Fig. S5. Colorimetric assay of PDAs derived from **PCDA-HBA 1** with various analytes: 1, Only PDAs; 2, PDAs + 100 μM NaF; 3, PDAs + 100 μM NaCl; 4, PDAs + 100 μM NaBr; 5, PDAs + 100 μM NaI.

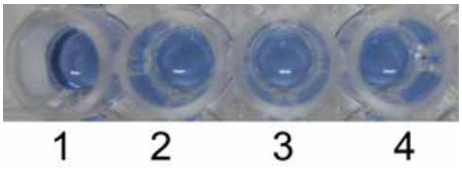


Fig. S6. Colorimetric assay of PDAs derived from **PCDA-HBA 1** with various analytes: 1, Only PDAs; 2, PDAs + 100 μM hexanol; 3, PDAs + 100 μM octanol; 4, PDAs + 100 μM decanol.

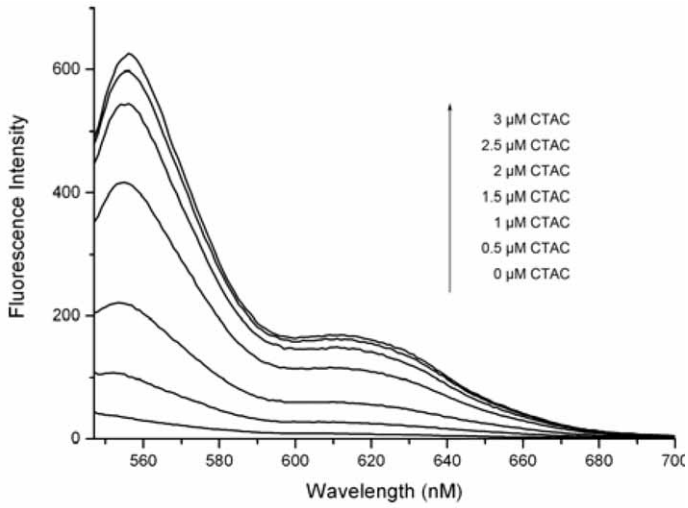


Fig. S7. Fluorescet titrations of **PCDA-HBA 1**-derived polymers (50 μM) with different amount CTAC.

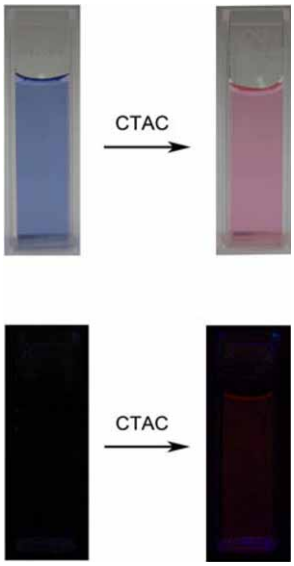


Fig. S8. The colorimetric and fluorescent images of PDAs in the absence and in the presence of CTAC.

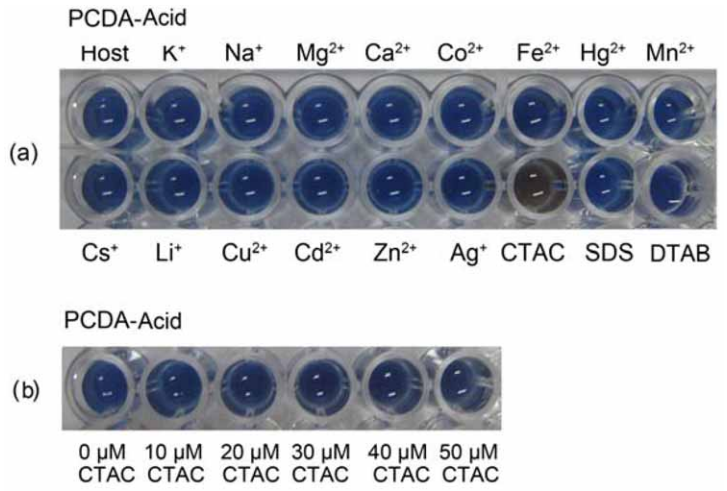


Fig. S9. (a) Colorimetric changes of **PCDA-Acid** (1 mM) with various analytes (100 μM) in HEPES-DMSO (9:1, v/v, 20 mM, pH 7.4). (b) Colorimetric titrations of **PCDA-Acid** (1 mM) with various concentrations CTAC in HEPES-DMSO (9:1, v/v, 20 mM, pH 7.4).

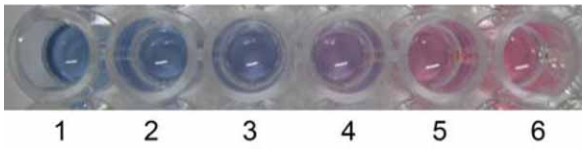


Fig. S10. Colorimetric responses of PDAs derived from the mixture of **PCDA-HBA 1** and **PCDA-HBA2** with different ratio: 1, **PCDA-HBA 1-HBA 1/ PCDA-HBA2** = 0/10, 2, **PCDA-HBA 1-HBA 1/ PCDA-HBA2** = 2/8; 3, **PCDA-HBA 1-HBA 1/ PCDA-HBA2** = 4/6; 4, **PCDA-HBA 1-HBA 1/ PCDA-HBA2** = 6/4; 5, **PCDA-HBA 1-HBA 1/ PCDA-HBA2** = 8/2; 6, **PCDA-HBA 1-HBA 1/ PCDA-HBA2** = 10/0.

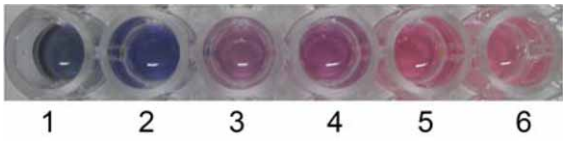


Fig. S11. Colorimetric responses of PDAs derived from the mixture of **PCDA-HBA 1**and **PCDA-Acid** with different ratio: 1, **PCDA-HBA 1-HBA 1/ PCDA-Acid** = 0/10, 2, **PCDA-HBA 1-HBA 1/ PCDA-Acid** = 2/8; 3, **PCDA-HBA 1-HBA 1/ PCDA-Acid** = 4/6; 4, **PCDA-HBA 1-HBA 1/ PCDA-Acid** = 6/4; 5, **PCDA-HBA 1-HBA 1/ PCDA-Acid** = 8/2; 6, **PCDA-HBA 1-HBA 1/ PCDA-Acid** = 10/0.