Supporting Information

A Multiple Switching Bisthienylethene and its Photochromic Fluorescent Organogelator

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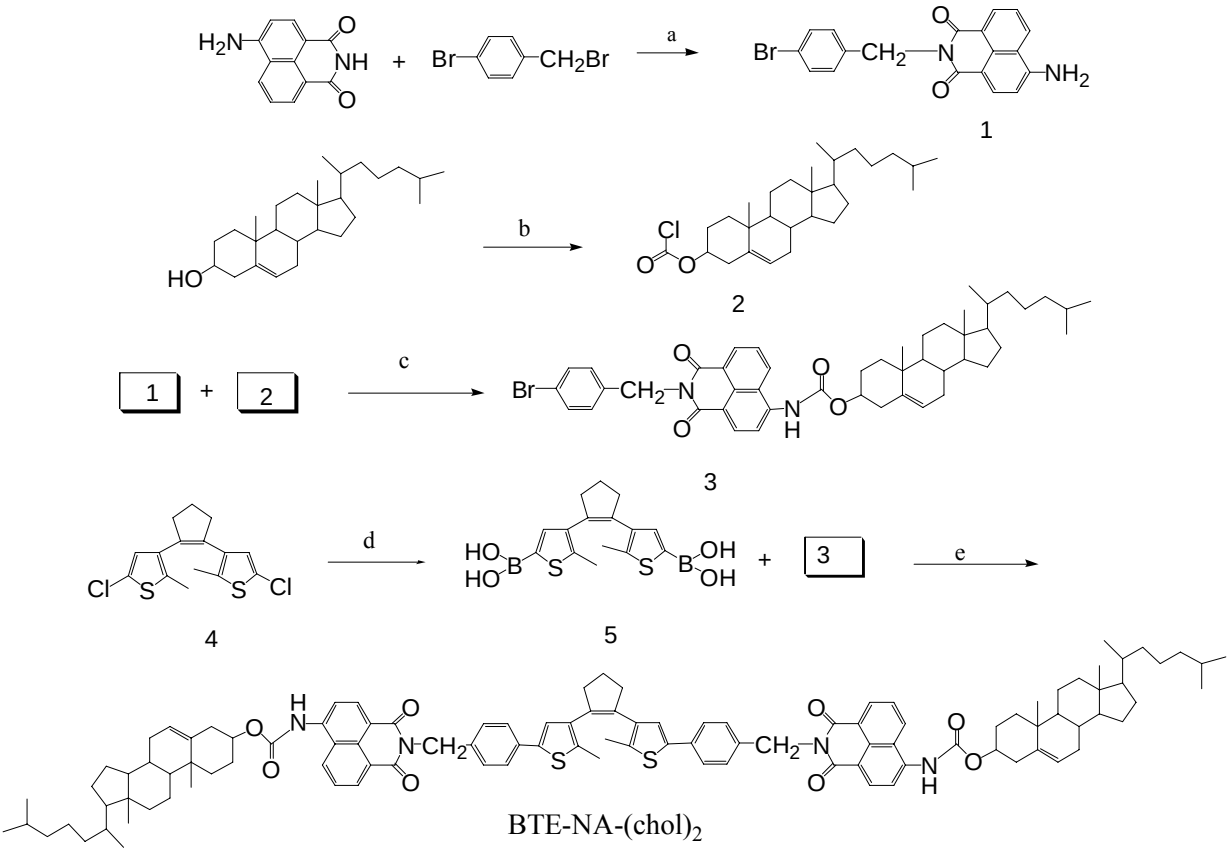
EXPERIMENTAL



Scheme S1 The synthetic routes of BTE-NA-$(chol)_2$ gel. (a) $NaOCH_3$, DMF, at room temperature, 24h, 85% yield; (b)$(COCl_2)_3$, CH_2Cl_2, 0-20ºC; (c) Dioxane, Et_3N, reflux，24h, 53% yield; (d)n-BuLi, −78ºC, $B(OBu)_3$, HCl, 63.8% yield; (e) $Pd(PPh_3)_4$, 20%$NaCO_3$, THF, 60ºC, 21% yield.

General Procedure. The ^{1}H NMR spectra were recorded on a Brucker AM-500 spectrometer. Chemical shifts were referenced to internal Me_4Si (TMS). The UV-Vis absorption spectra and fluorescence spectra were obtained on a Varian Cary 500 spectrometer and a Varian Cary Eclipse, respectively. Mass spectra were obtained by a HITACHI-80 instrument. The photochromic reactions were carried out using the light of a CHF-XM 500-W high-pressure mercury lamp that passed through suitable filters in a sealed Ar-saturated 1-cm quartz cell. Scanning electron microscopy (SEM) images of xerogels were obtained using a JEOL JSM-6360 scanning electron microscope.

Gelation test: The gelator and the solvent were put in a septum-capped test tube and heated until the solid was dissolved. The sample vial was cooled in air to room temperature, and then left for 1 h at this temperature. The states of the materials were evaluated by the "stable-to-inversion of a test tube" method. A gel in a sealed glass tube was inverted, strapped to a thermometer near the bulb, and immersed in a stirred water bath at room temperature. The temperature of the bath was raised slowly and the range of T_{gel} was taken from the point at which the first part of the gel was observed to fall to the point at which all had fallen under the influence of gravity.

SEM measurements: The gel was put on a carbon-coated copper grid and dried in vacuo for 12 h at room temperature (the gel was prepared from toluene/Ethanol (1:3 v/v)), For SEM observation; the xerogels were shielded by Au and examined with a JEOL JSM-6360 scanning electron microscope. The accelerating voltage of SEM was 15 kV.

The synthesis of 1-Bromo-4- methylbenzene), 4-(6-amino-4-yl-1H, 3H-benzo[de]) isoquinolin(1)

A solution of the 4-amino-1, 8-naphthalimide (7.0g, 33mmol) in 120 ml anhydrous DMF was treated with solution of $NaOCH_3$ (2M in Ethanol solution, 16.5ml) dropwise over 5min at room temperature under argon atmosphere. The above solution was stirred for 12 hour then the solution of 1-bromo-4-(bromomethyl)benzene(12.3g, 49.5mmol) in anhydrous 15ml DMF was added and the reaction continually stirred 5 hour. The product was poured into 500ml water and filtrated and dried affording of the crude product as a yellow solid. The crude product was further purified by recrystallization with anhydrous Ethanol and obtained the yellow purified product. (10.7g, 85% yield).

^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ = 4.96 (br, 2H, -NH_2-), 5.30 (s, 2H, -CH_2-), 7.42 (d, J = 8.7 Hz, 2H, Ph-H), 7.40 (d, J = 8.6 Hz, 2 H, Ph-H), 6.89(d, J = 8.16 Hz, 1 H, naphthalene-H), 7.66 (t, J_1 = 7.55Hz, J_2 = 8.15Hz, 1 H, naphthalene-H), 8.1 (d, J = 8.3 Hz, 1H, naphthalene-H), 8.43 (d, J = 8.1 Hz, 1H, naphthalene-H), 8.6 (d, J = 7.2Hz, 1 H, naphthalene-H) Anal. Calcd. for $C_{19}H_{13}BrN_2O_2$ (380.02) TOF-MS (EI) m/z: 380.0 (M^+).

The synthesis of Cholesteryl –Carbonchrolide(2)

The cholesterol (7.74 g, 20mmol) were dissolved in 60 ml of dry dichloromethane and stirred for 30min at room temperature. Then triphosgene (2.0g, 6.7mmol) and drops of pyridine were added at 0 °C by an ice bath. The reaction mixture then was stirred for 1 h at 0 °C and 3 h at room temperature. After the reaction finished, the solvent was evaporated and the product was used in the next reaction without any workup.

The synthesis of 1-Bromo-4- methylbenzene), 4-(6-Cholesteryl –Carbonacidamide o-4-yl-1H, 3H-benzo[de]) isoquinolin(3)

A solution of the compound **1** (3.82g, 10mmol) and the compound **2**(6.72g, 15mmol) in 40mL

dioxane was heated under reflux for 24 hour. After the mixture was cooled to ambient temperature, the solvent was distilled off under reduced pressure. The residue was poured into water and filtered to obtain the crude product. The resulting solid was purified by column chromatography on silica (CH_2Cl_2/petroleum=3:1v/v) to yield a yellowish solid, and yellowish solid was crystallized with anhydrous Ethanol to afford **3** (4.2 g, 53% yield) as pale-yellowish solid.

^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ = 1.06-2.48 (m, 43H cholesterol-H), 5.44(s, 1H, C=CH-), 5.31(s, 2H, -NCH_2), 4.72(m, 1H, -COOCH-) 7.42 (d, J = 8.7 Hz, 2H, Ph-H), 7.40 (d, J = 8.8 Hz, 2 H, Ph-H), 7.77 (t, J_1 = 7.4Hz, J_2 = 8.3Hz, 1 H, naphthalene-H), 7.41 (d, J = 8.2 Hz, 1H, naphthalene-H).8.20 (d, J = 8.5 Hz, 1H, naphthalene-H), 8.42(d, J = 8.3 Hz, 1H, naphthalene-H), 8.63 (d, J = 7.22Hz, 1 H, naphthalene-H), 8.65 (1 H, -NHCOO-) Anal. Calcd. for $C_{47}H_{57}BrN_2O_4$ (793.35). TOF-MS (ESI) m/z: 795.7 (M^++H+1).

1,2-Bis(5-boronic acid-2-methyl-3-thienyl)cyclopentene (5)

To a stirred solution of compound 4 (2 g, 6mmol) in THF (20 ml) at -78 °C under argon atmosphere in the absence of light was added dropwise 1.6 M n-BuLi in hexane (0.78 g, 12mmol), and the reaction mixture was stirred at -78 °C for a further 30 min. To the reaction mixture was quickly added tributyl borate (2.76 g, 12mmol) by syringe, and the reaction mixture was stirred at room temperature for 15 h. To the reaction mixture was added CH_2Cl_2 (30 ml) and HCl (15 ml, 3 M). The phases were separated and the organic phase was extracted with 15 ml of 10% NaOH aqueous solution three times. The combined aqueous phase was acidified with 10% HCl. The gray precipitate was collected by filtration and washed with water. Drying of the white powder in vacuum gave 1.34 g of compound 1 in yield of 63.8%.

^{1}H NMR (500 MHz, $CDCl_3$, ppm): 8.02(s, 4H, –OH), 7.42(s, 2H, thienyl C–H), 2.75(t, 4H,

–CH_2–), 2.02(m, 2H, –CH_2–), 1.76(s, 6H, –CH_3).

The synthesis of, 1,2-Bis{5-[2-(4- ethylbenzene, 4-(6-Cholesteryl –Carbonacidamide -4-yl-1,3-dioxo-1H,3H-benzo[de])isoqu-inolin)-2-methyl-3-thienyl]cyclopentene(BTE-NA-(chol)$_2$)

The compound **3** (1.586g, 2 mmol) was dissolved in the mixture solvent 30ml (THF-benzene =3/1v/v), $Pd(PPh_3)_4$ (100mg) was added, and the resulting was stirred for 15 min at room temperature. Then aqueous Na_2CO_3 (1ml, 2 M) was added. The reactive mixture was heated and refluxed at a temperature of 60 ºC and the THF solution of 4(0.3g, 1mmol)nwas added dropwise via a syringe. Subsequently the mixture was refluxed for 12 h and cooled to room temperature. The reactive mixture was poured into H_2O and extracted with CH_2Cl_2 The organic layer was separated and dried (anhydrous Mg_2SO_4). After concentration, the compound was purified by column chromatography on silica (CH_2Cl_2/hexane=3:1v/v) to yield a buff solid powder (0.35g, 21% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.04-2.70 (m, 98H, CH, CH_2, CH_3), 4.63(m, 2H, cholesterol -COOCH-), 5.36(s, 2H, cholesterol -C=CH-), 5.30 (s, 4H, -NCH_2), 6.85 (s, 2 H, thiophene-H), 7.32 (d, J = 8.1 Hz, 4H, Ph-H), 7.42 (d, J = 8.3 Hz, 4 H, Ph-H), 7.36 (d, J = 8.1 Hz, 2 H, naphthalene-H), 7.62(t, J_1 = 7.7Hz, J_2 = 7.8Hz, 2 H, naphthalene-H), 8.1 (d, J = 8.52Hz, 2 H, naphthalene-H), 8.30 (d, J = 8.3 Hz, 2H, naphthalene-H), 8.51 (d, J = 7.97Hz, 2H, naphthalene-H), 8.53 (2 H, -NHCOO-).

Anal. Calcd. for $C_{109}H_{128}N_4S_2O_8$ (1686.0) MALDI-TOF-MS: found m/z: 1687.6587(M^++H).

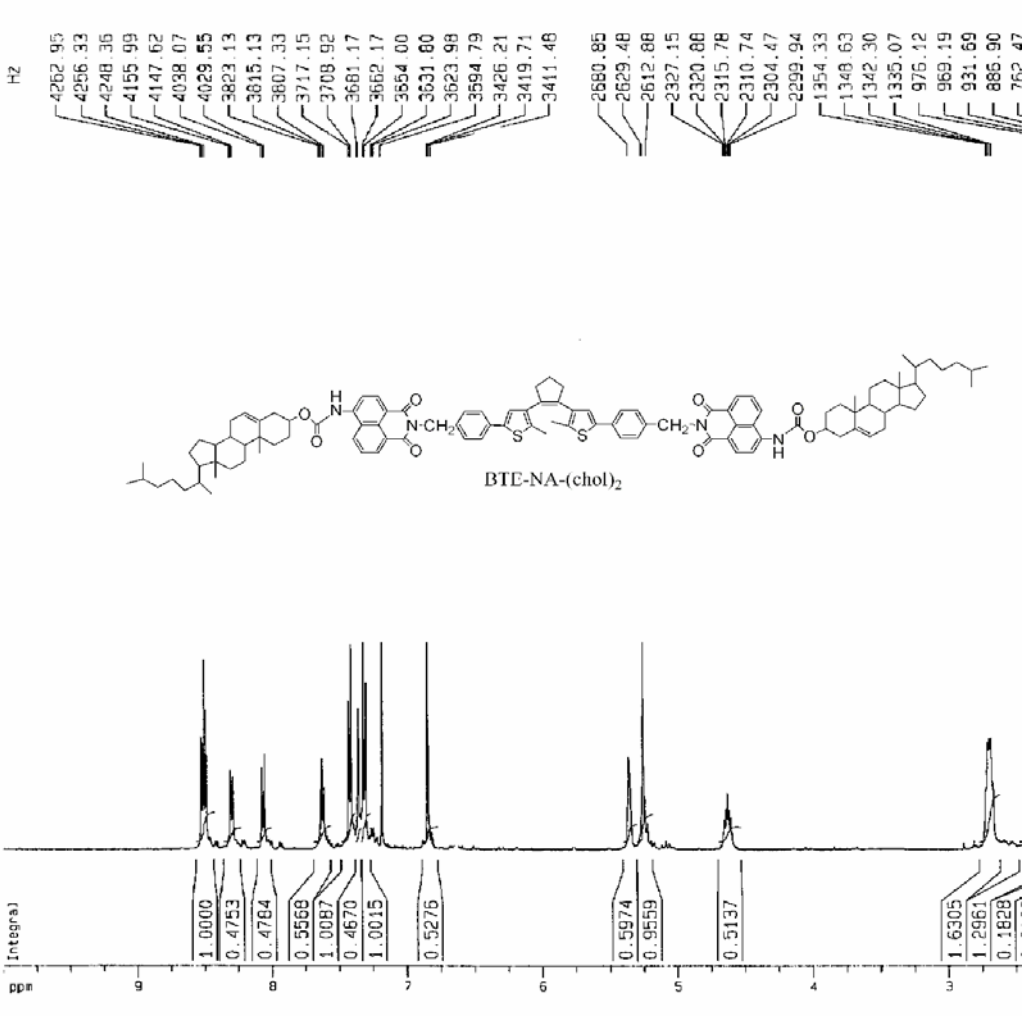


Figure S1. Selective ^{1}H NMR data of BTE-NA-(chol)$_2$ in Scheme 1

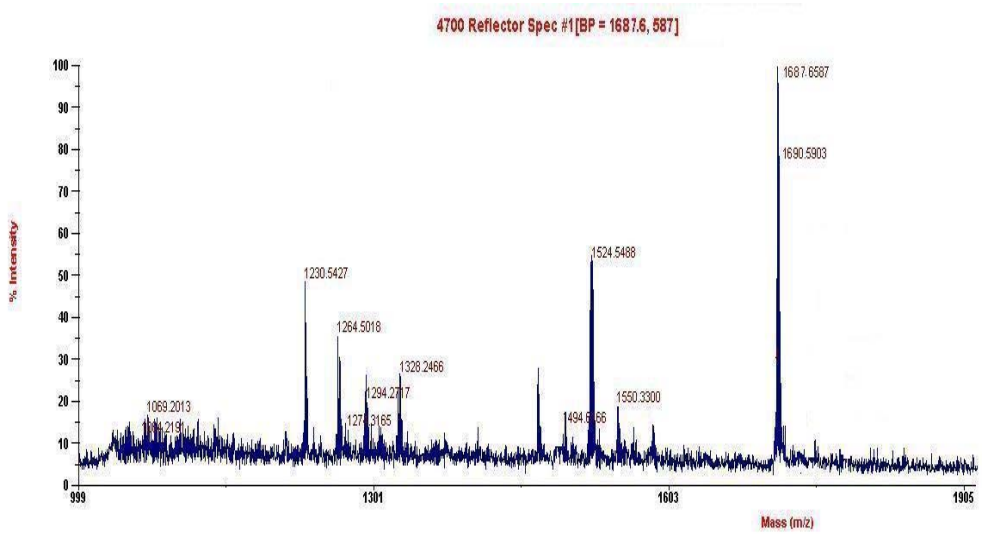


Figure S2. MALDI-TOF-MS data of BTE-NA-(chol)$_2$ in Scheme 1.

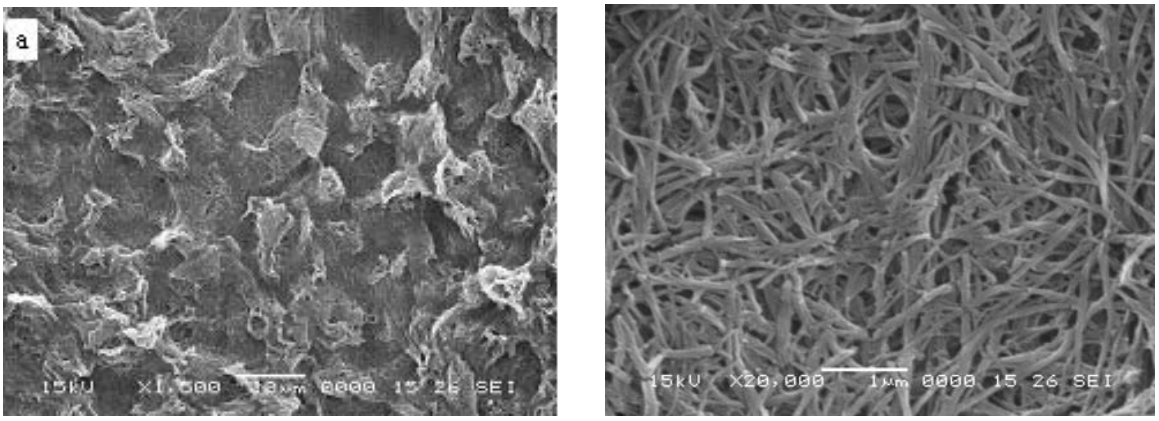


Figure S3. SEM images of BTE-NA-$(chol)_2$ gel (The gels were prepared from the toluene/Ethanol(1:3v/v), [BTE-NA-$(chol)_2$]=0.5 wt %).

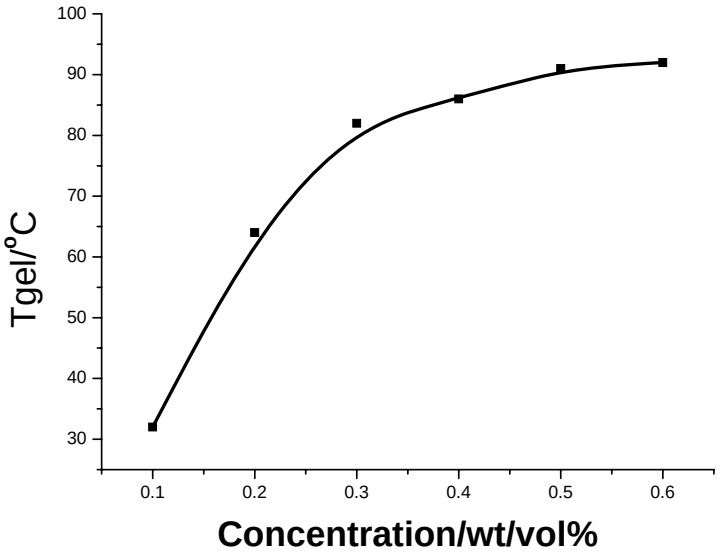


Figure S4 Gel-to-sol phase transition temperature as the BTE-NA-$(chol)_2$ concentration in mixed solvent of the toluene/1-butanol (1:3v/v).

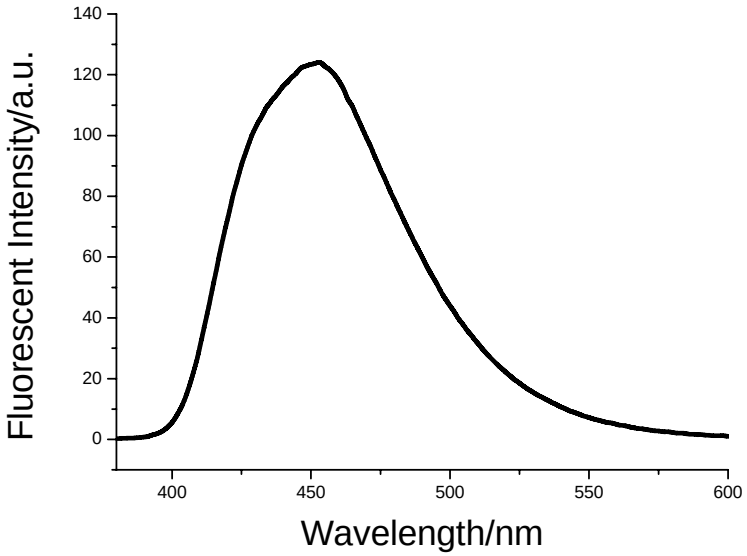


Figure S5 The fluorescent emission spectrum of compound **3** (2.0×10^{-5}mol/L) in THF at room temperature.

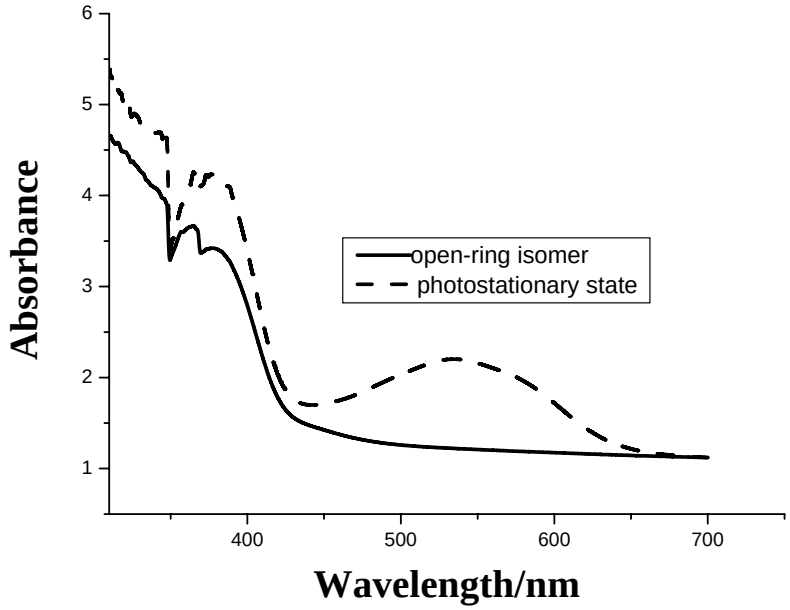


Figure S6a Absorption spectra of BTE-NA-$(chol)_2$ gel, the open-ring isomer (—), in the photostationary state(------) (0.5 wt/v %) upon irradiation by 365nm light at room temperature.

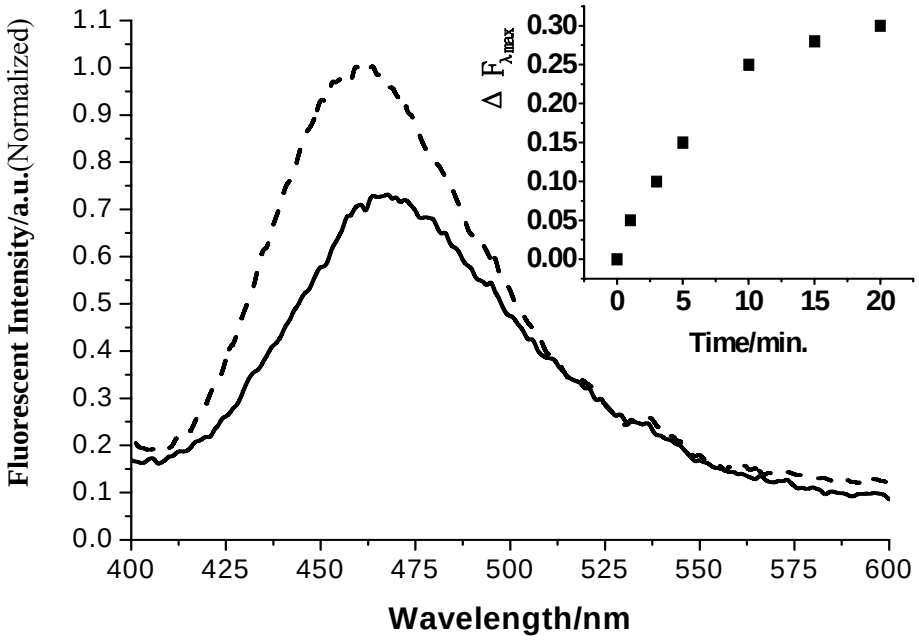
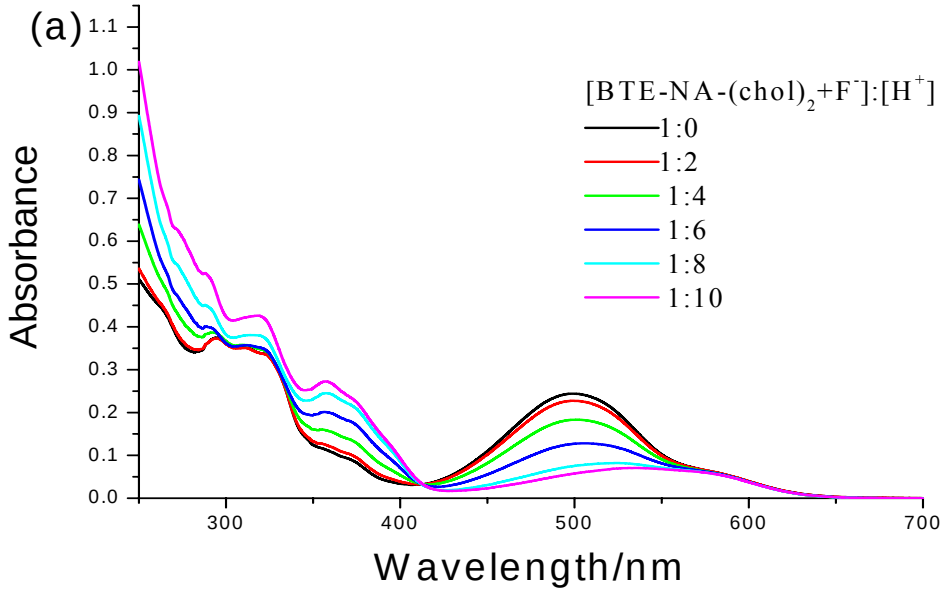


Figure S6b Fluorescent spectra (excited at 355 nm) of the BTE-NA-$(chol)_2$ gel, the open-ring isomer (—), in the photostationary state(------) (0.5 wt/v %) upon irradiation by 365nm light at room temperature. Inset curves show the fluorescent change value at maximum emission wavelength with irradiation times.



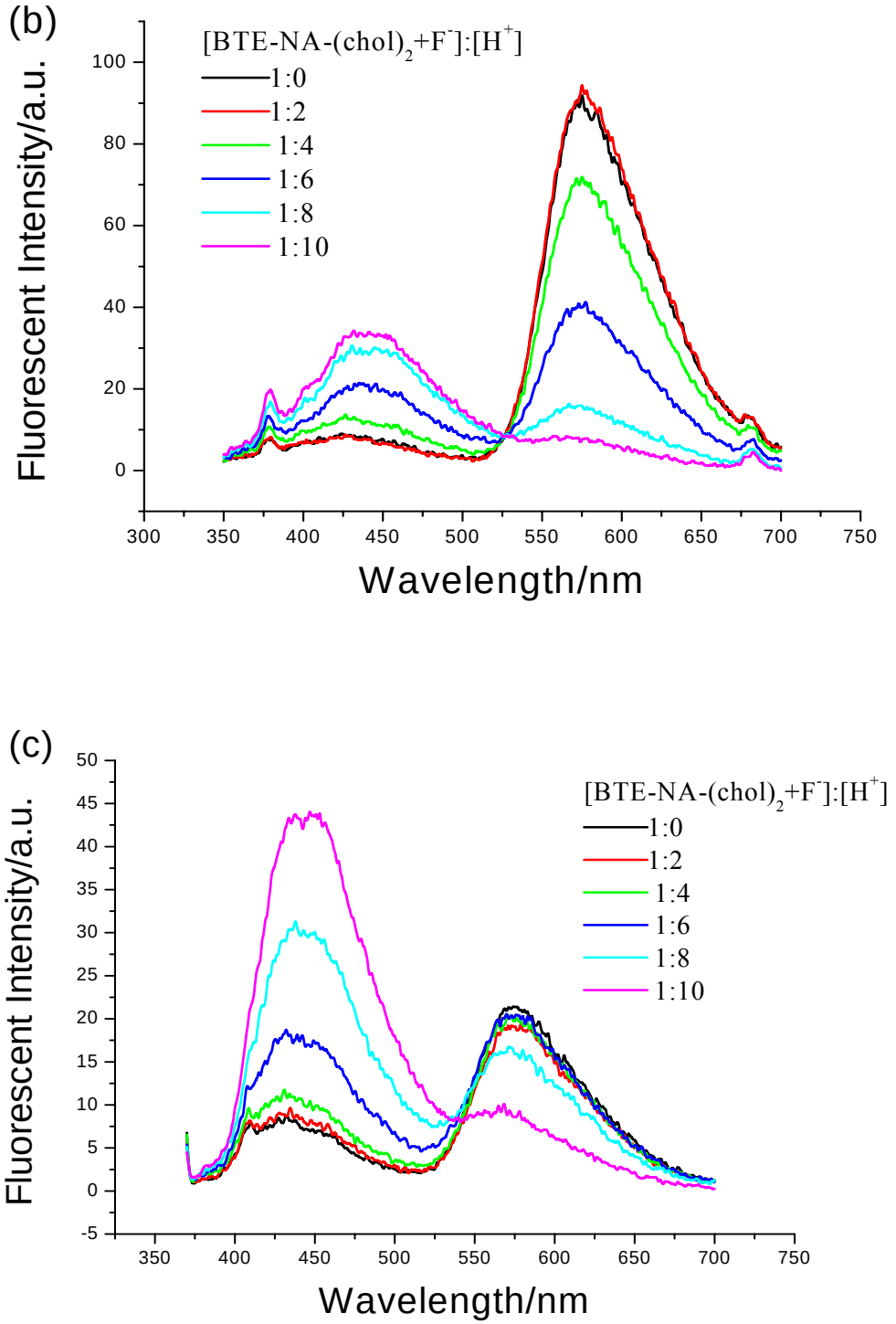


Figure S7 (a) The changes in absorption of closed form of BTE-NA-(chol)$_2$ titration with F^- [Sol+F^-(closed)](2.0×10^{-5}mol/L) titration with proton in THF. (b) The changes in fluorescent emission spectra (excited at 345 nm) of the closed form of BTE-NA-(chol)$_2$ titration with F^- [Sol+F^- (closed)] (2.0×10^{-5}mol/L) titration with proton in THF. (c) The changes in fluorescent emission spectra (excited at 365 nm) of the closed form of BTE-NA-(chol)$_2$ titration with F^- [Sol+F^- (closed)] (2.0×10^{-5}mol/L) titration with proton in THF.

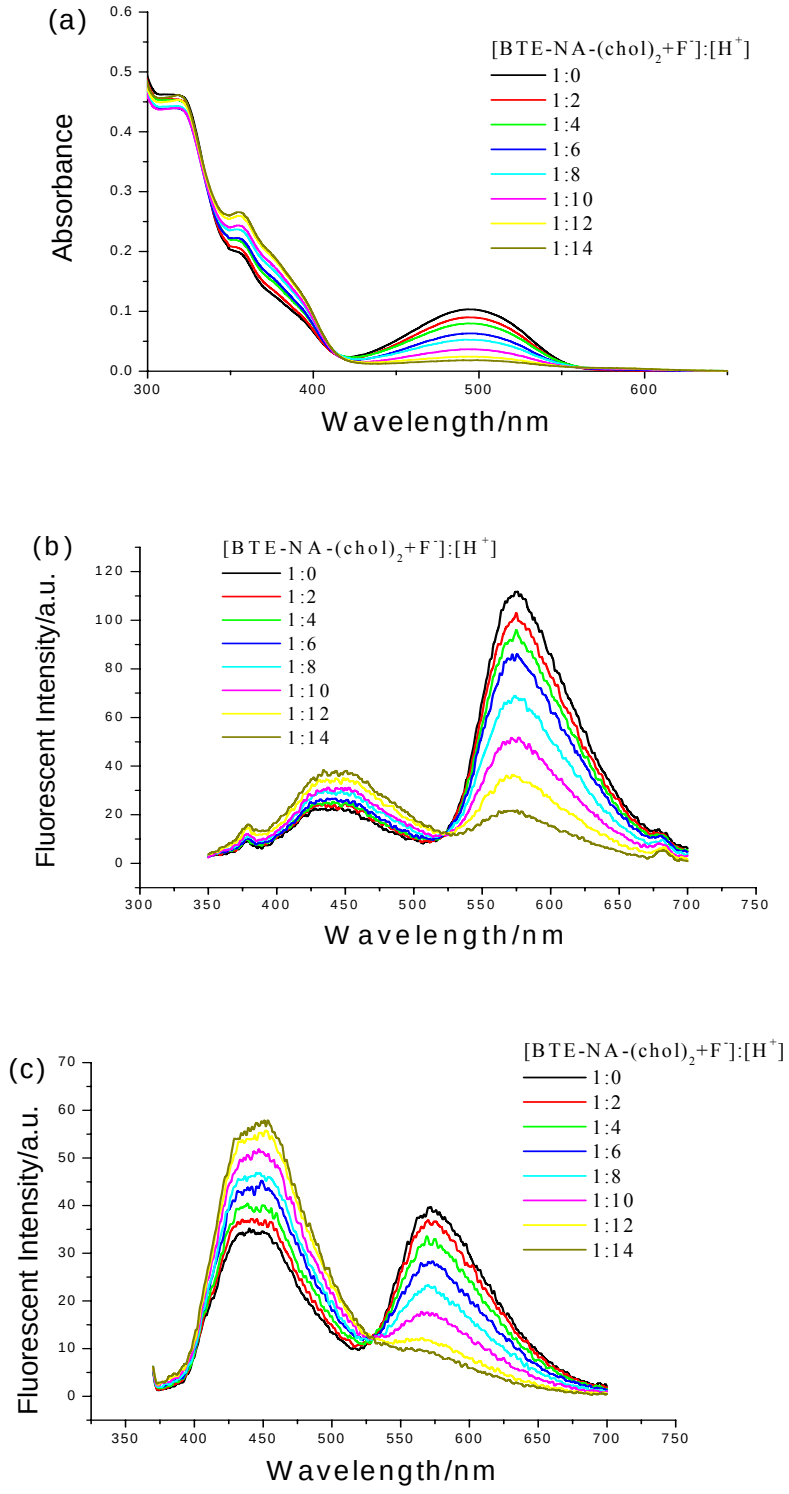


Figure S8 (a) The changes in absorption of the open form of BTE-NA-$(chol)_2$ titration with F^- [Sol+F^- (open)] (2.0×10^{-5}mol/L) titration with proton in THF. (b) The changes in fluorescent emission spectra (excited at 345 nm) of the open form of BTE-NA-$(chol)_2$ titration with F^- [Sol+F^- (open)] (2.0×10^{-5}mol/L) titration with proton in THF. (c) The changes in fluorescent emission spectra (excited at 365 nm) of the open form of BTE-NA-$(chol)_2$ titration with F^- [Sol+F^- (open)] (2.0×10^{-5}mol/L) titration with proton in THF.

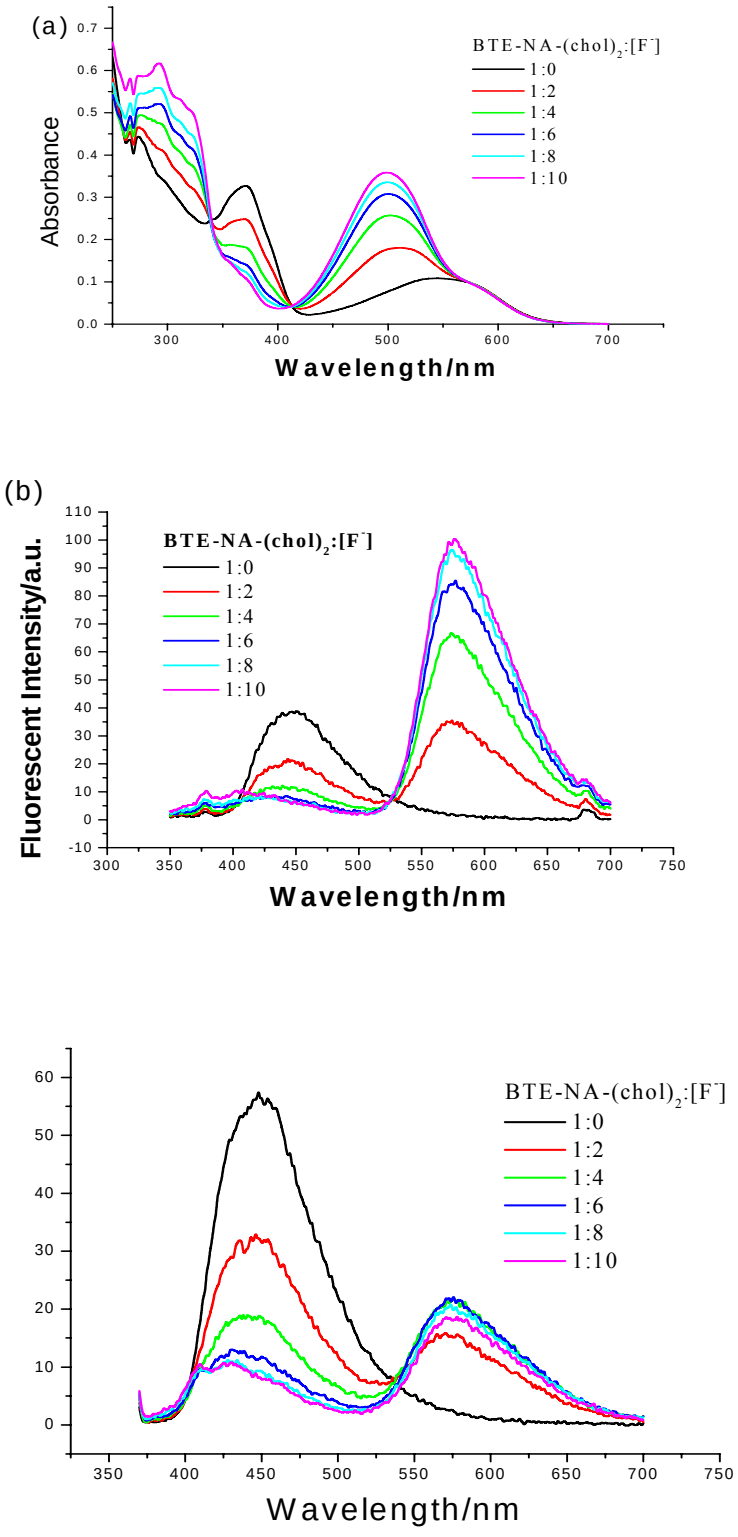


Figure S9 (a) The changes in absorption of the closed form of BTE-NA-(chol)$_2$ [Sol (closed)] (2.0×10^{-5}mol/L) titration with F^- in THF. (b) The changes in fluorescent emission spectra (excited at 345 nm) of the closed form of BTE-NA-(chol)$_2$ [Sol (closed)] (2.0×10^{-5}mol/L) titration with F^- in THF. (c) The changes in fluorescent emission spectra(excited at 365 nm) of the closed form of BTE-NA-(chol)$_2$ [Sol (closed)] (2.0×10^{-5}mol/L) titration with F^- in THF.