Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C
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Supporting Information

A guanidine derivative of naphthalimide with excited-state deprotonation coupled intramolecular charge transfer property and its application

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1. pKa measurement

The ground state pK_a values of ENG and TNG were determined by the change of absorbance 350 nm upon the pH changing from 5.78-11.2. The absorbance at 350 nm was plotted versus pH value of buffer. The excited state pKa values of ENG and TNG were determined by the change of the fluorescence intensity at 580 nm (excited at 350 nm) upon the pH changing from 0.3-3.38. The fluorescence intensity at 580 nm was plotted versus pH value of buffer. pKa values were calculated according to the following equation:

$pK_a = pH_x + \lg [(A_{HB}^{+} - A_x)/(A_x - A_B)]$ Or $pK_a^{*} = pH_x + \lg [(I_B - I_x)/(I_x - I_{HB}^{+})]$.

where, A_{HB}^{+}, A_X and A_B represent the absorbance of absolute acid form, the absorbance at the pH chosen and the absorbance of absolute base form respectively. I_B, I_x, I_{BH}^{+} the represent the fluorescence intensity at absolute base form, the fluorescence intensity at the pH chosen and the fluorescence intensity of absolute acid form respectively. The pKa values are derived from the nonlinear curve-fitting of these data (Originpro 8.0).

The ground-state pKa was calculated to be 8.53 ± 0.03 as shown in Figure S1a. The pKa^{*} in the excited state is calculated to be 0.895 ± 0.03 as shown in Figure S1b.

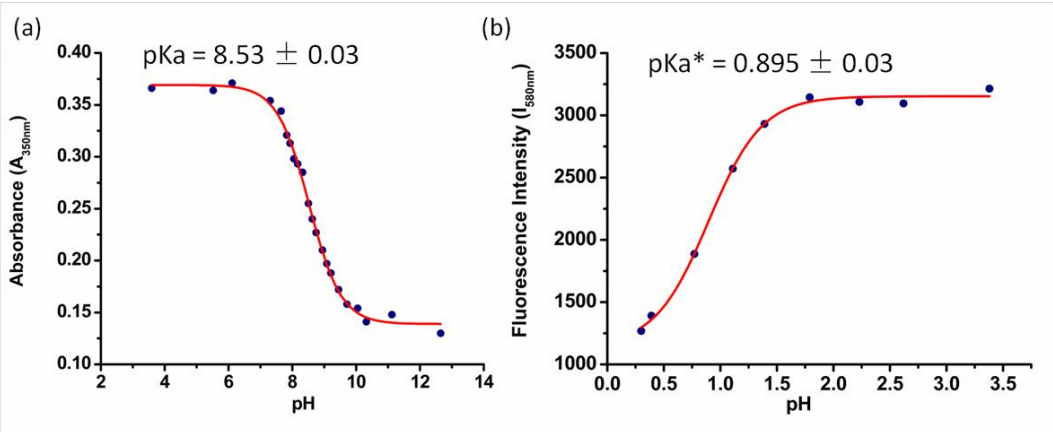


Figure S1. The response curve of ENG to pH: (a) absorbance change at 350 nm with pH values in the range of pH 5.78-11.14; (b) fluorescence intensity change at 580 nm (λ_{ex} = 350 nm) with pH value in the range of pH 0.3-3.38.

2. Comparison of the ^{1}H NMR spectrum of ENG in acidic state and basic state

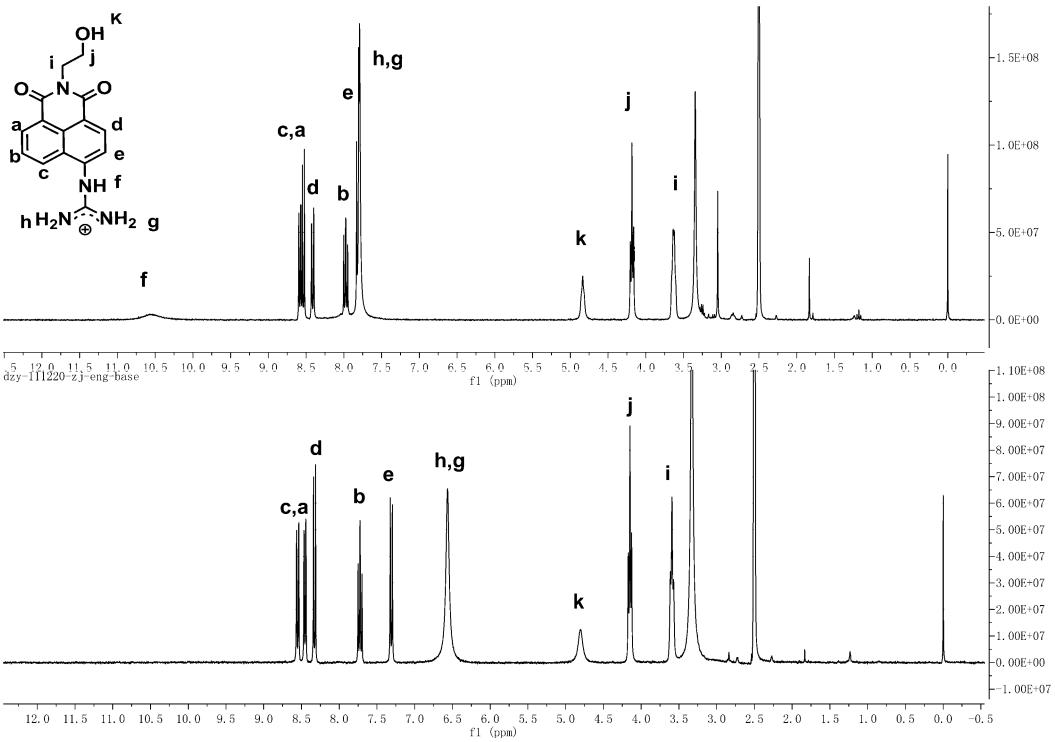


Figure S2. ^{1}H NMR spectra of ENG taken in a DMSO-d_6 acid form (the top) and basic form (the bottom).

3. Fluorescence properties of TNG

The changes of fluorescence intensity and wavelength of TNG upon the pH changing are similar with that of ENG as shown in Figure S3. In the pH range from 4.0-12.0, the emission band around 470 nm decreased with the pH increase, while the emission band around 580 nm did not changed much. In the more acid environment, the emission band around 580 nm decreased upon the pH decrease. As shown in Figure S3 b and d, the pKa at the ground state is calculated to be 8.49 ± 0.1 and the pKa* in the excited state is calculated to be 0.904 ± 0.08.

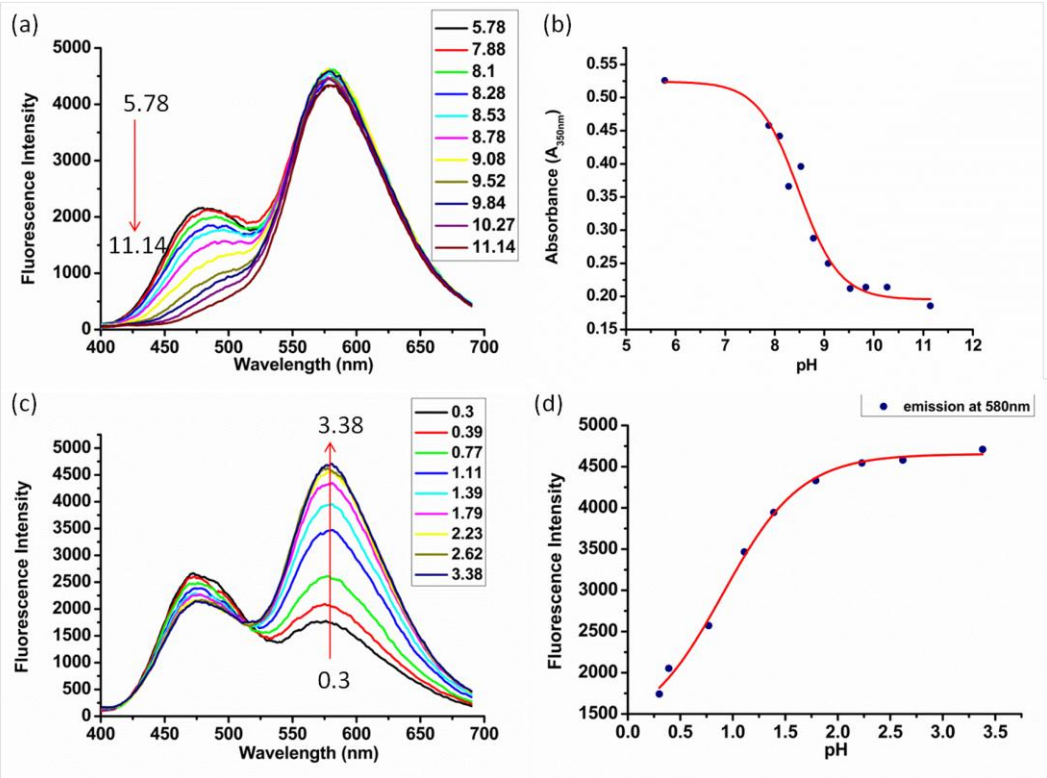


Figure S3. (a) Fluorescence spectra obtained in Glycine-HCl-NaOH buffer at pH 5.78, 7.88, 8.10, 8.28, 8.53, 8.78, 9.08, 9.52, 9.84, 10.27, 11.14, excited at 365 nm; (b) The pH response curve of absorbance at 350 nm from pH 5.78-11.14; (c) Fluorescence spectra measured in Glycine-HCl buffer at pH 0.3, 0.39, 0.77, 1.11, 1.39, 1.79, 2.33, 2.62, 3.38, excited at 350 nm; (d) The pH response curve of fluorescence intensity at 580 nm from pH 0.3-3.38.

The excitation and emission spectra of TNG in different solvents are similar with that of ENG. Different from ENG, TNG has a butyl substitution at 9-position (imide N atom) of naphthalimides. These phenomena indicate that the different substituent group in N-9 of naphthalimide can't affect their fluorescence properties and the hydroxyl group of hydroxyethyl don't involve the proton transfer.

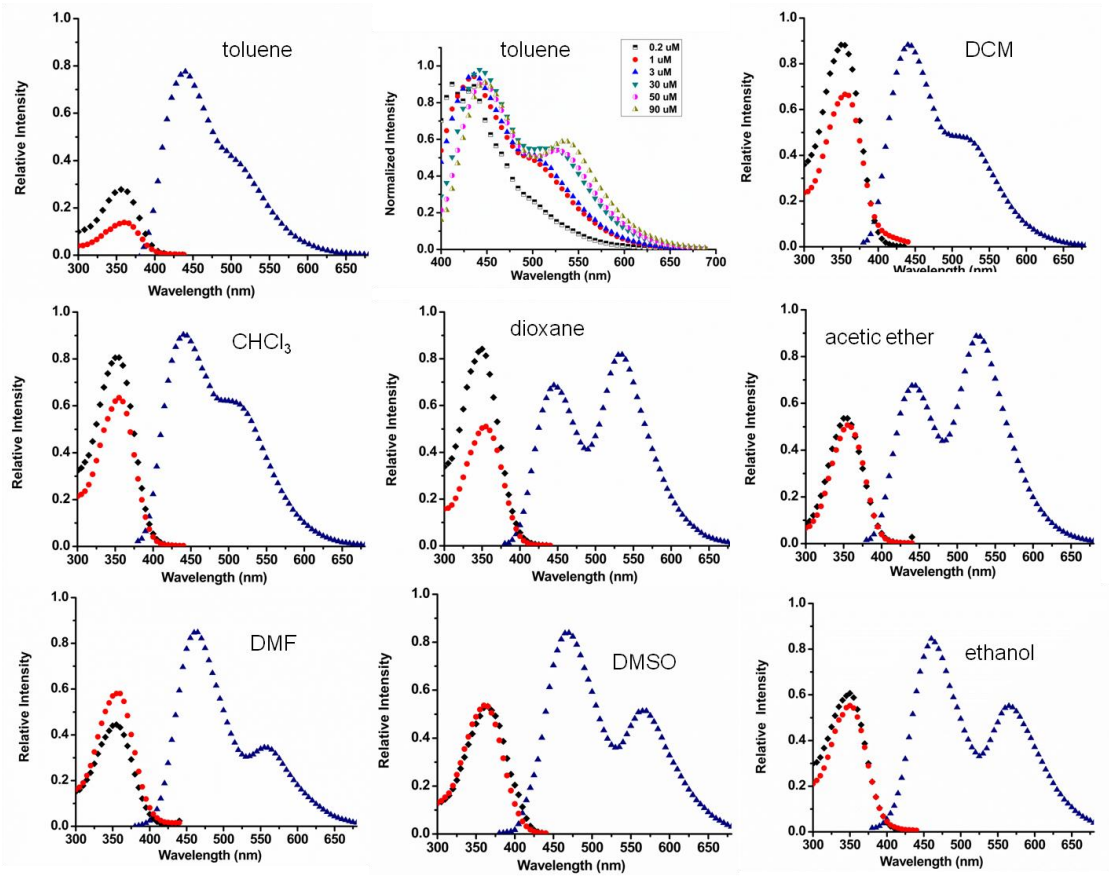


Figure S4. Static excitation and fluorescence spectras of TNG in different solvent; as figures show the solvent are toluene, the increase of concentration of ENG in toluene, DCM, $CHCl_3$, acetone, dioxane, acetic ether, DMF, DMSO, ethanol; fluorescence spectrum excited at 350 nm (up triangle dot), excitation spectrum spectrum detected at 460 nm (diamond dot) and excitation spectrum detected at 600 nm (circle dot).

4. Φ_f: fluorescence quantum yield

The fluorescence quantum yields in different solvents have been determined on the basis of the absorption and fluorescence spectra of the probe. The quinine sulfate (purchased from jk-chemical company) was used as standard with $\Phi_f = 0.54 \pm 0.02$ (in 1.0 N sulfuric acid). Where A_{ref}, F_{ref}, n_{ref} and A_{sample}, F_{sample}, n_{sample} represent the absorbance at the exited wavelength, the integrated emission band area and the solvent refractive index of the standard and the sample, it follows a formula like this:

$$\Phi_{sample} = \Phi_{ref} \times (A_{ref} \times F_{sample})/(A_{sample} \times F_{ref}) \times (n^2_{sample}/n^2_{ref})$$

5. Absorption spectra of ENG in different surfactant systems

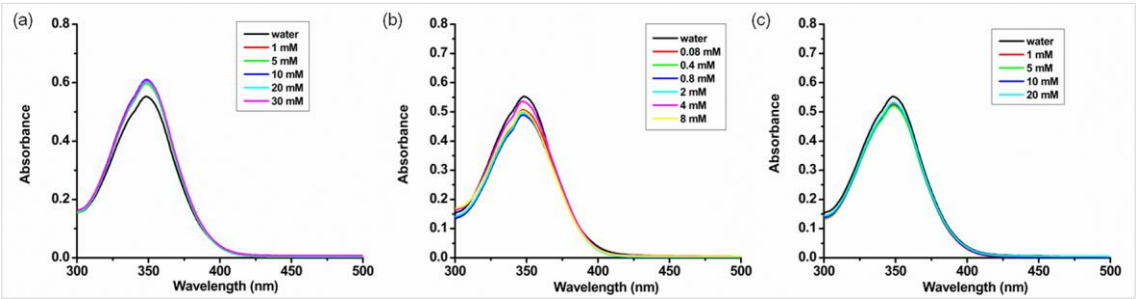


Figure S5. Absorption spectra of ENG (50 μM) in different concentration of surfactants: (a) Triton X-100 solution; (b) CTAB solution; (c) SDS solution.

6. Luminescence of ENG in different solvents

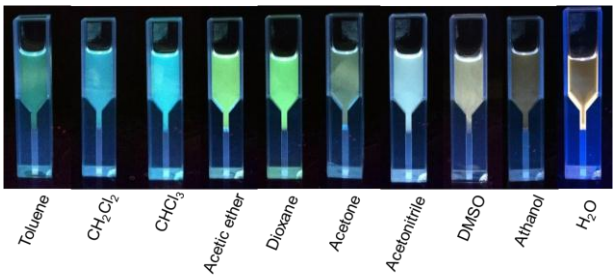


Figure S6. Change of the fluorescence emission observed in different solvents, excitation under 300 nm transmission of UV light source. From left to right are ENG (5 μM, 2.5 μM, 2.5 μM, 5 μM, 5 μM, 5 μM, 5 μM, 5μM, 10μM, 50 μM) in toluene, dichloromethane, chloroform, acetic ether, Dioxane, acetone, acetonitrile, DMSO, ethanol, and H_2O.

7. Spectral change of ENG with the addition of F^-

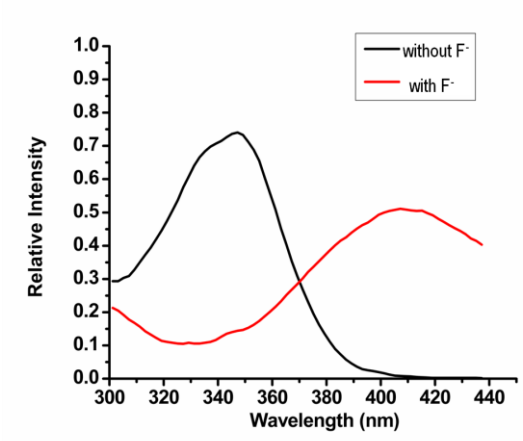


Figure S7. Static excitation spectra of ENG in CH_3CN: excitation spectrum detected at 450 nm (black line) in the absence of F^- and excitation spectrum detected at 560 nm (red line) in the presence of 10 μM F^- (TBAF).

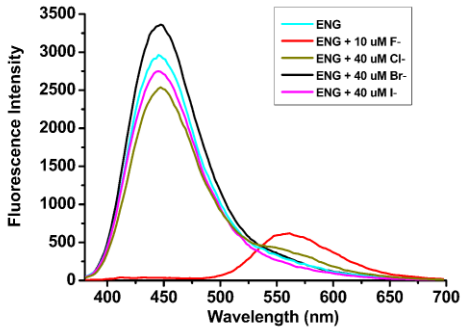


Figure S8. Fluorescence spectral change of ENG (4 μM) in CH_3CN with the addition of different halide anions: 10 μM F^-, 40 μM Cl^-, 40 μM Br^-, 10 μM I^-, with excitation of 365 nm.

8. Response of ENG to the addition of F^-

The emission intensity at 457 nm shows a linear response to F^- in the range of 0.75–1.75 μM with a detection limit of 0.28 μM calculated by fluorescence titration. The linear equation: y = -563.4x + 1334.5, R^2 = 0.996. The apparent equilibrium dissociation constant (Kd) between ENG and F^- in acetic ether was calculated to be 0.45 ± 0.02 μM based on the curve of fluorescence change at 457 nm (Sigma plot 10.0).

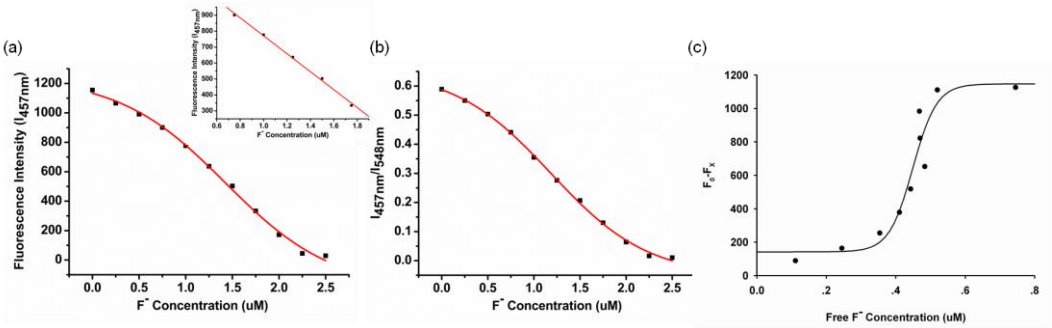


Figure S9. (a) Fluorescence intensity change of ENG in acetic ether solution with different concentration of F^- (TBAF) 0-2.5 μM (Ex/Em: 375/457 nm), Inset: linear response plot of emission intensity versus F^- (0.75-1.75 μM); (b) Fluorescence intensity ratio of ENG at 457 and 548 nm with excitation at 375 nm; (c) Plot of the fluorescence decrease (457 nm) versus concentration of free F^- for the determination of Kd.

The emission intensity at 445 nm show a linear response to F^- in the range of 0–5 μM with a detection limit of 68 nM calculated by fluorescence titration. The linear equation: y = -578.06x + 3799.9, R^2 = 0.996. (Origin 8.0) The apparent Kd between ENG and F^- in acetonitrile was calculated to be 0.78 ± 0.07 μM based on the curve of fluorescence change at 445 nm (Sigma plot 10.0)

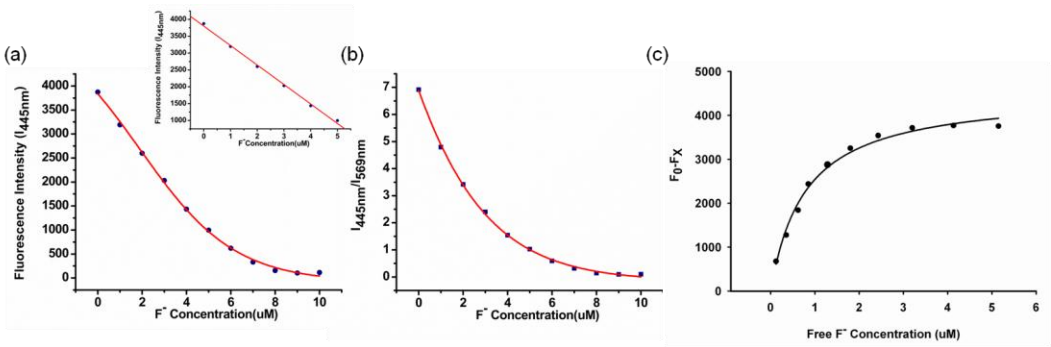
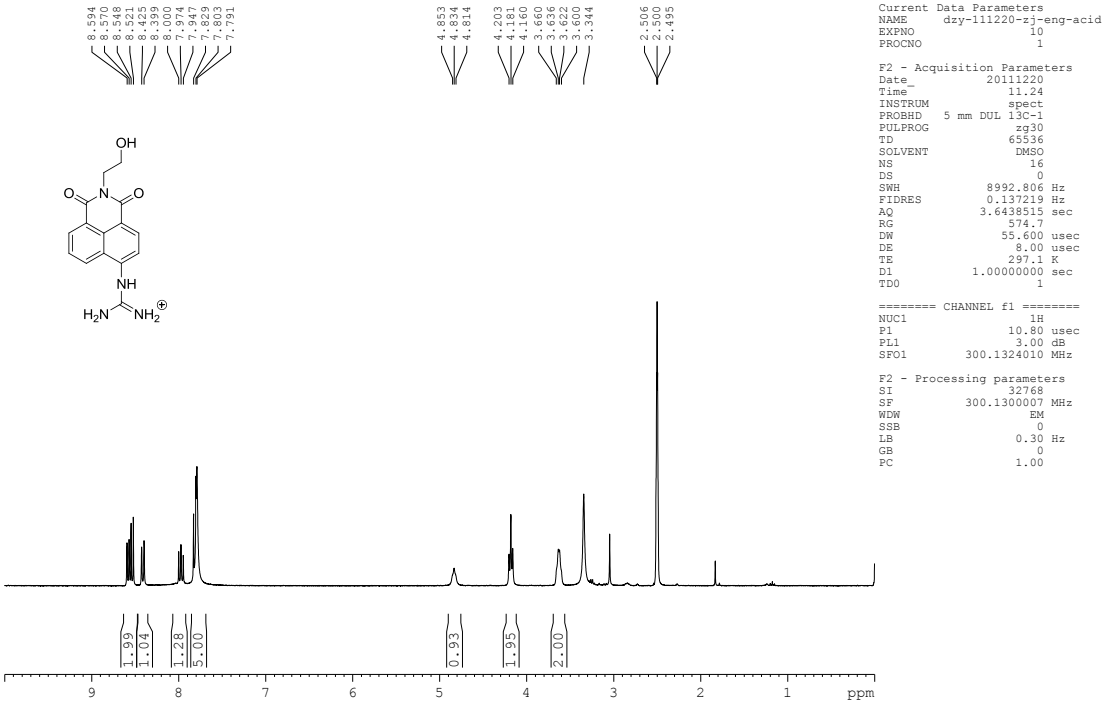
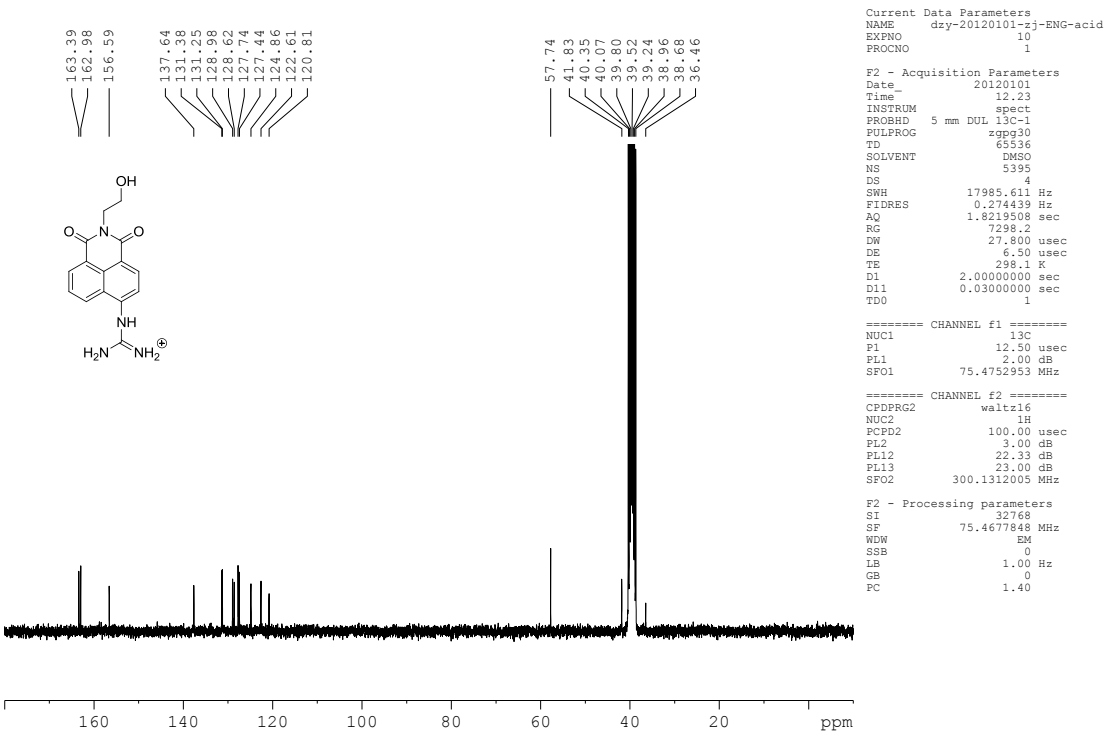


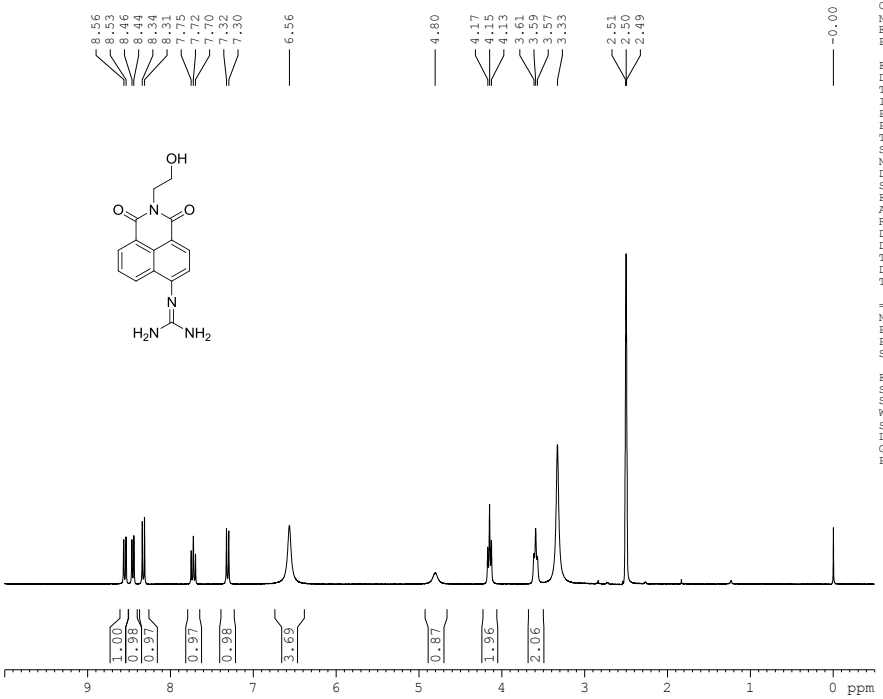
Figure S10. (a) Fluorescence intensity change of ENG in acetonitrile solution with different concentration of F^- (TBAF) 0-10 μM (Ex/Em: 365/445 nm), Inset: linear plot plot of emission intensity versus F (0–5 μM); (b) Fluorescence intensity ratio of ENG at 445 and 569 nm with excitation at 365 nm; (c) Plot of the fluorescence decrease (445 nm) versus concentration of free F^- for the determination of Kd.

9. Structure Characterization Figures

1 H NMR spectra





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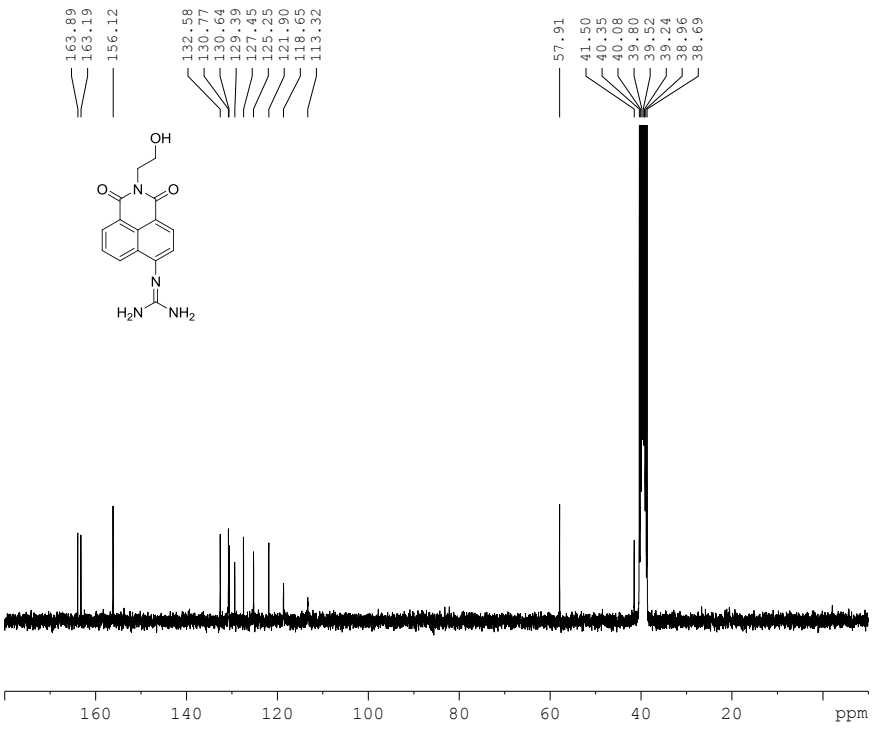


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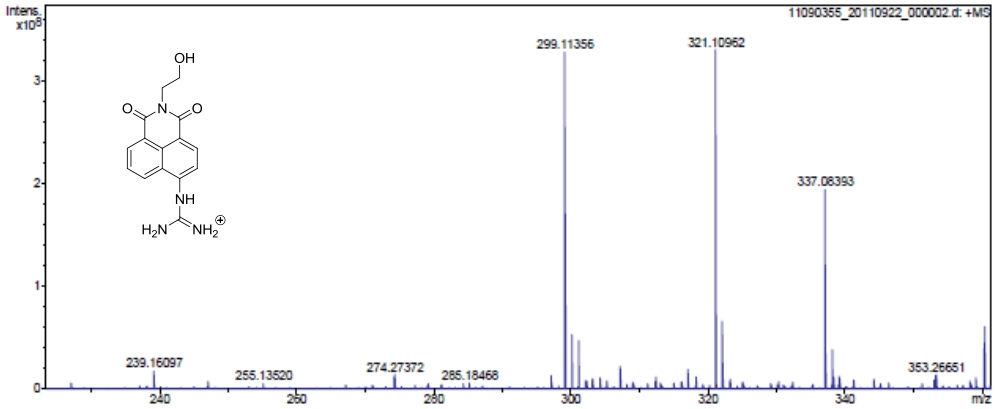

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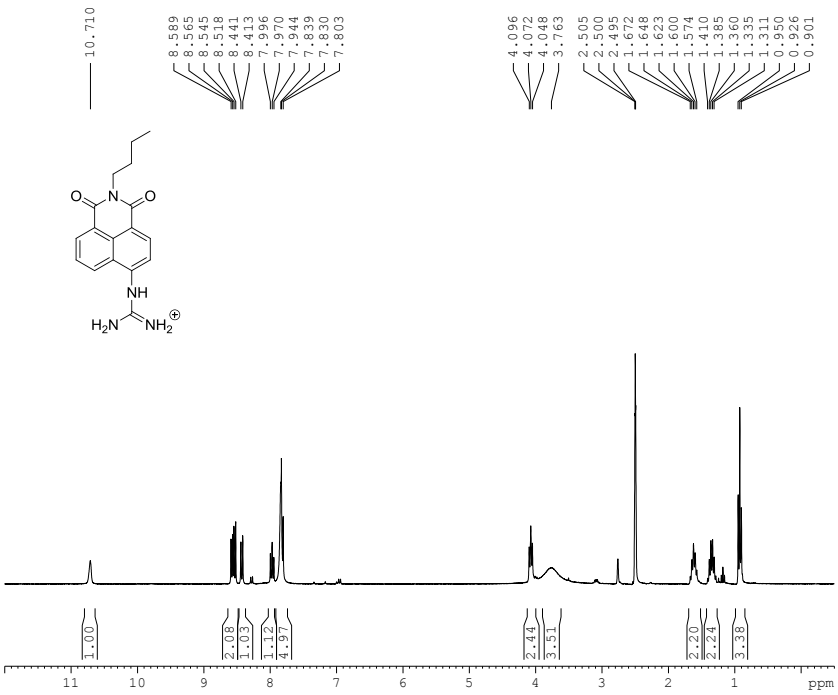


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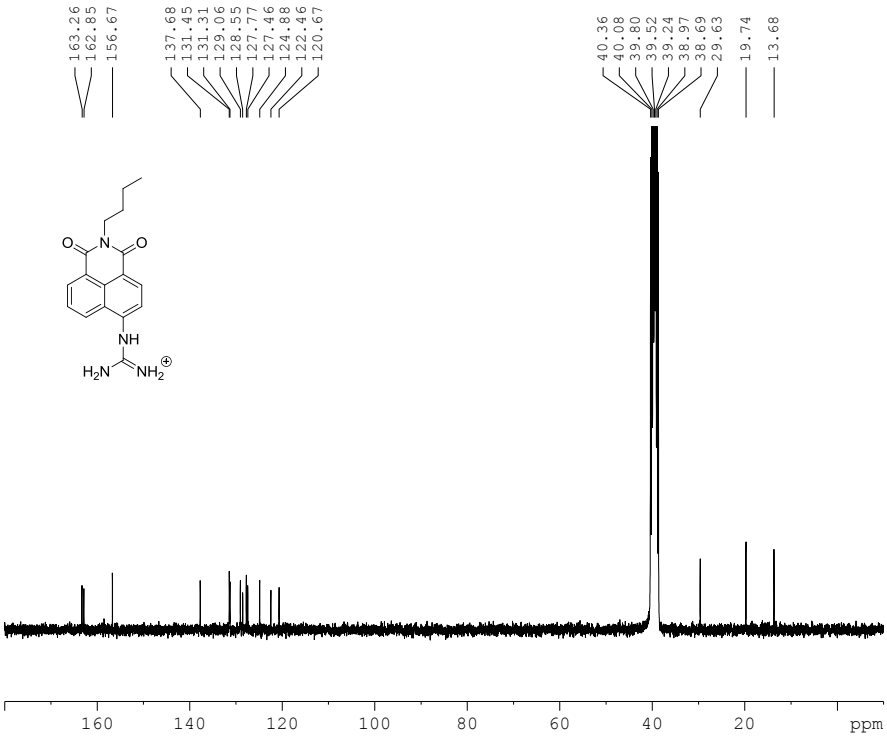


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