

Supporting Information for  
**Amphiphilic B, O-chelated aza-BODIPY dye: synthesis, pH-sensitivity and aggregation behaviour in H<sub>2</sub>O/DMSO mixed solvent**

Bin Lei,<sup>a</sup> Hongfei Pan,<sup>a</sup> Yongjie Zhang,<sup>a</sup> Xiang-Kui Ren<sup>a,b</sup> and Zhijian Chen<sup>\*a,b</sup>

<sup>a</sup> *School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China*

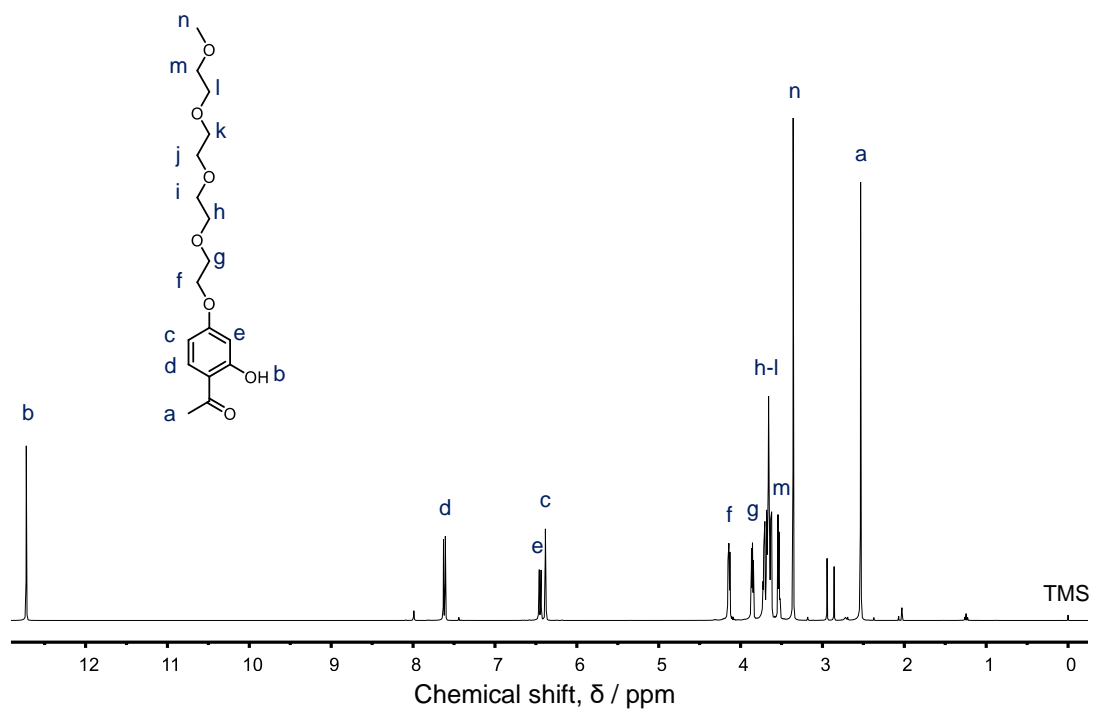
<sup>b</sup> *Collaborative Innovation Center of Chemical Science and Chemical Engineering, Tianjin University, Tianjin 300072, China*

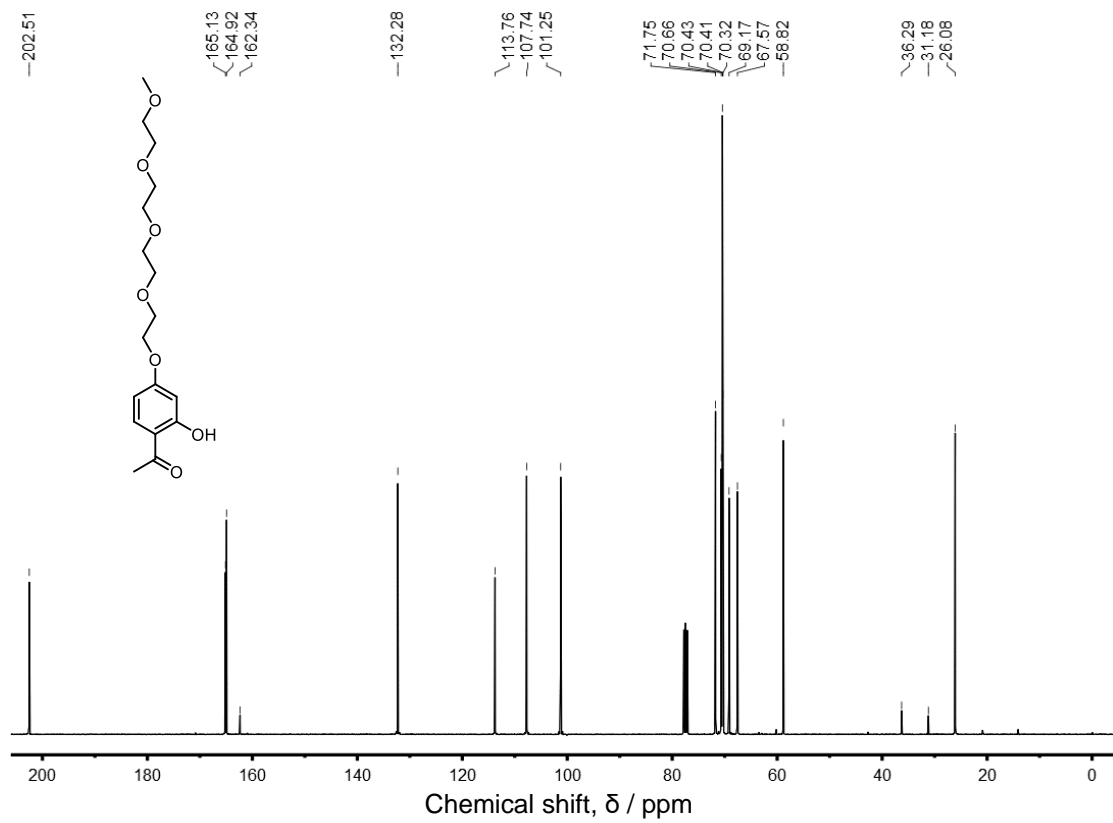
*E-mail addresses: zjchen@tju.edu.cn (Z. Chen)*

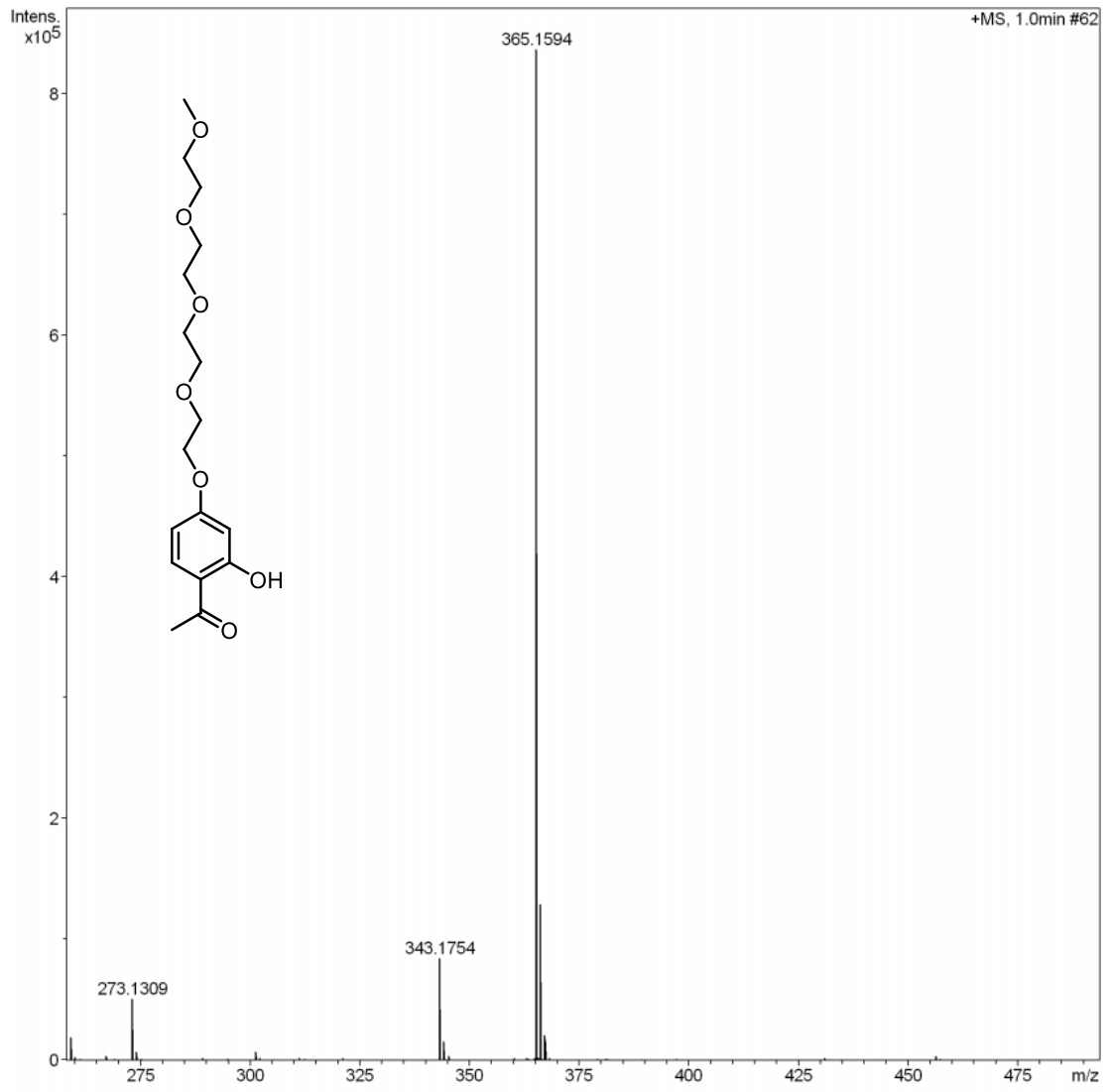
**Table of contents**

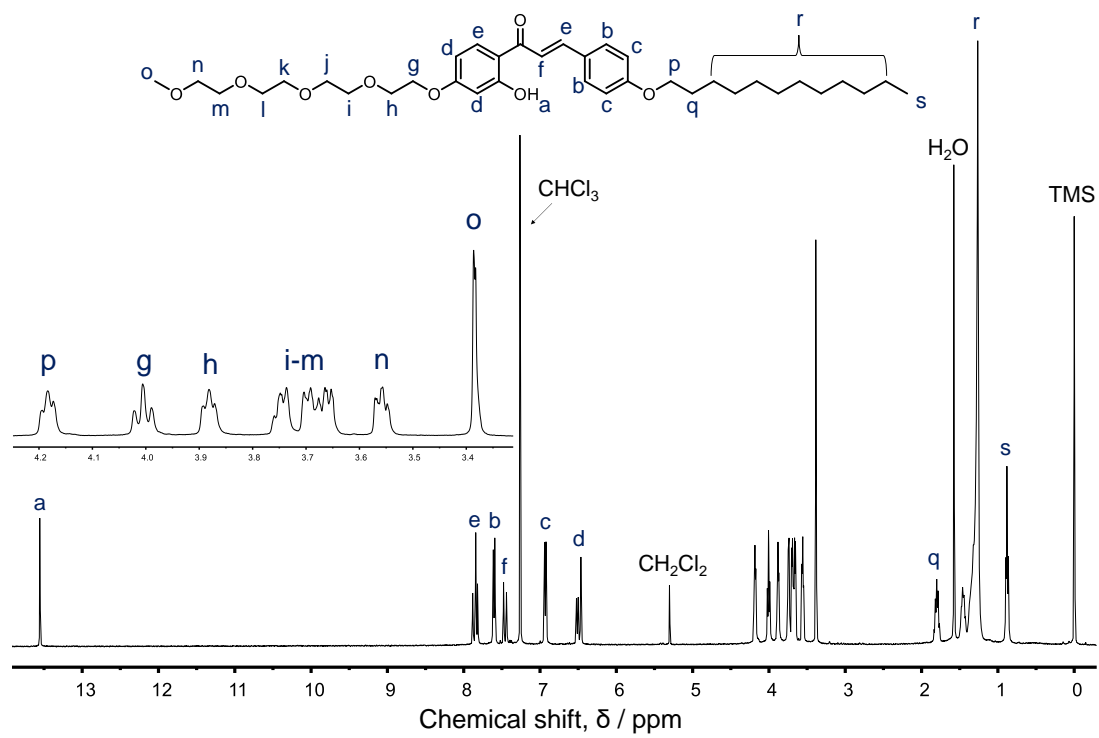
1. NMR and mass spectra of compounds <b>1-6</b> .....	S1
2. Vis/NIR absorption and fluorescence spectra of <b>1</b> and mass spectrum of <b>2·H<sup>+</sup></b> .....	S17
3. Studies on thermodynamic aggregation properties and molecular packing.....	S25
4. Calculation of pK <sub>a</sub> for <b>2·H<sup>+</sup></b> .....	S28
5. References.....	S29

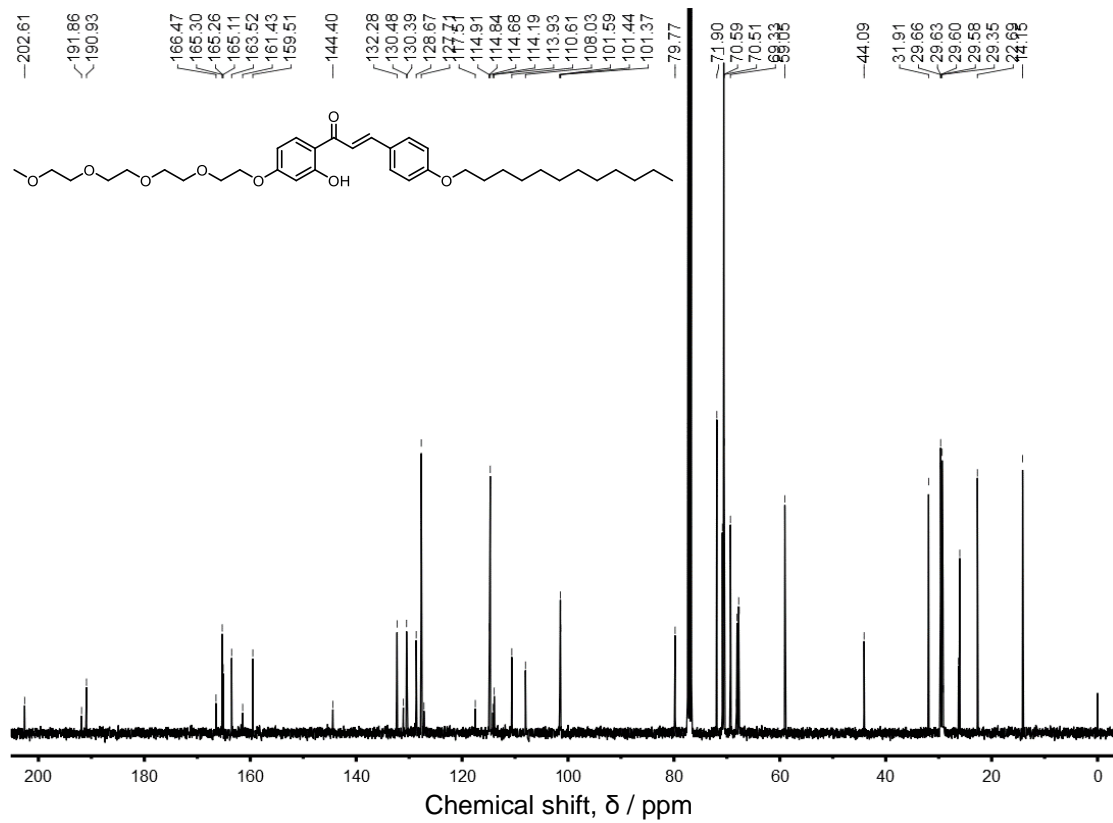


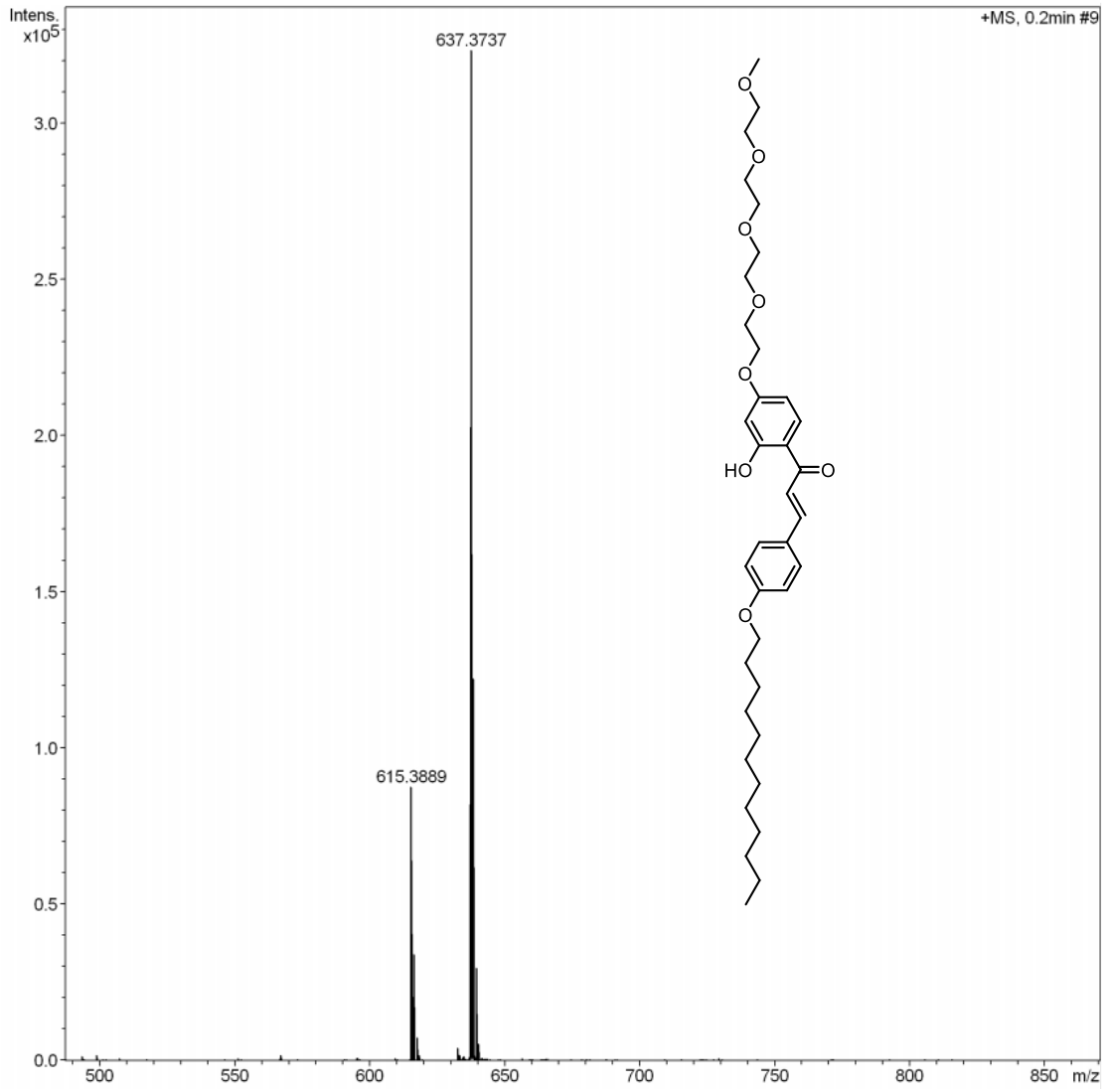




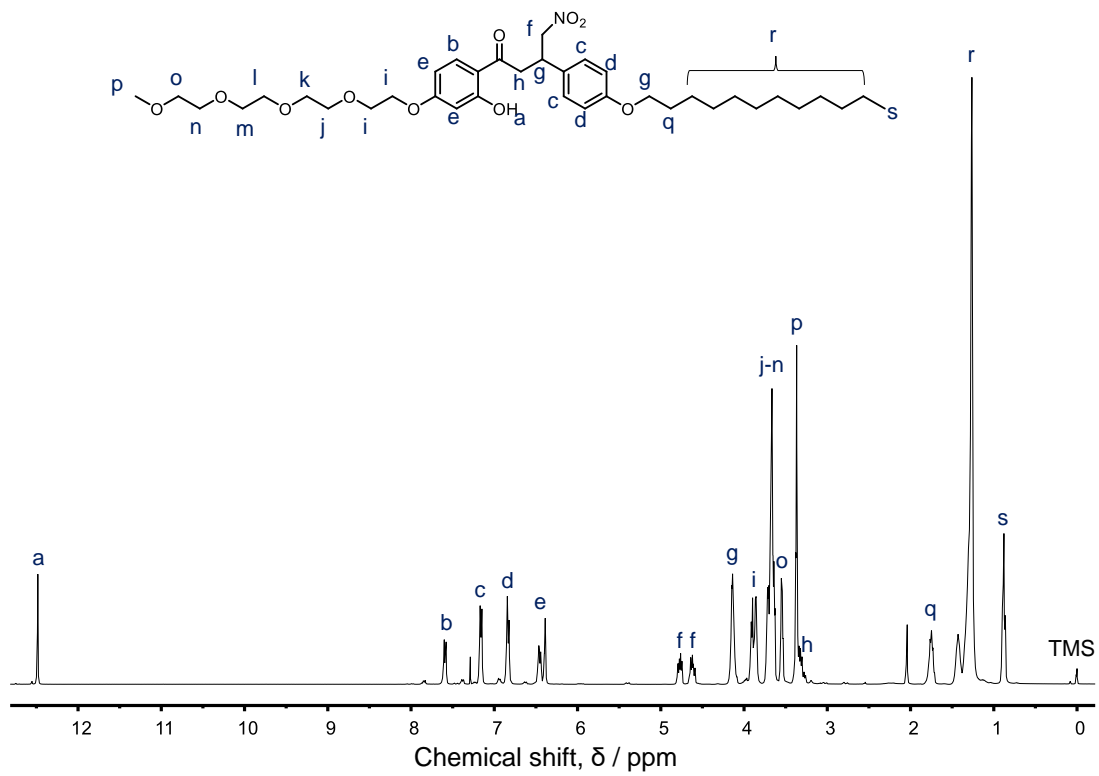


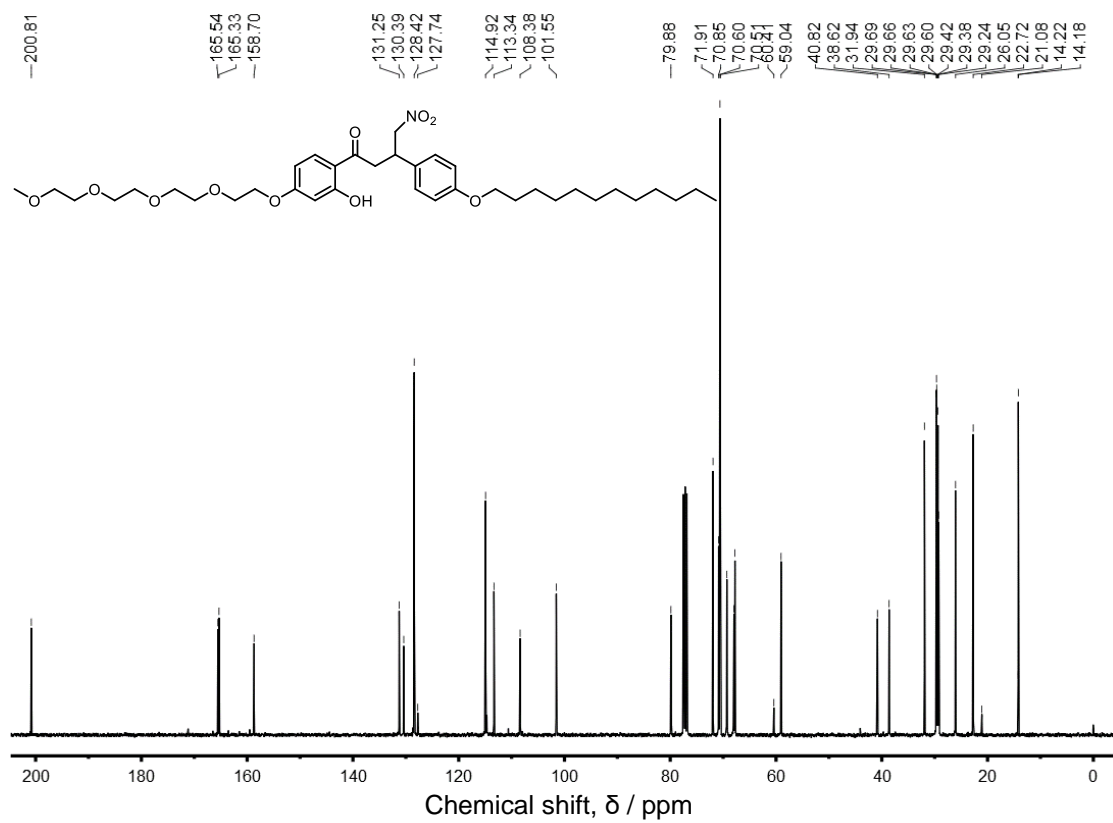




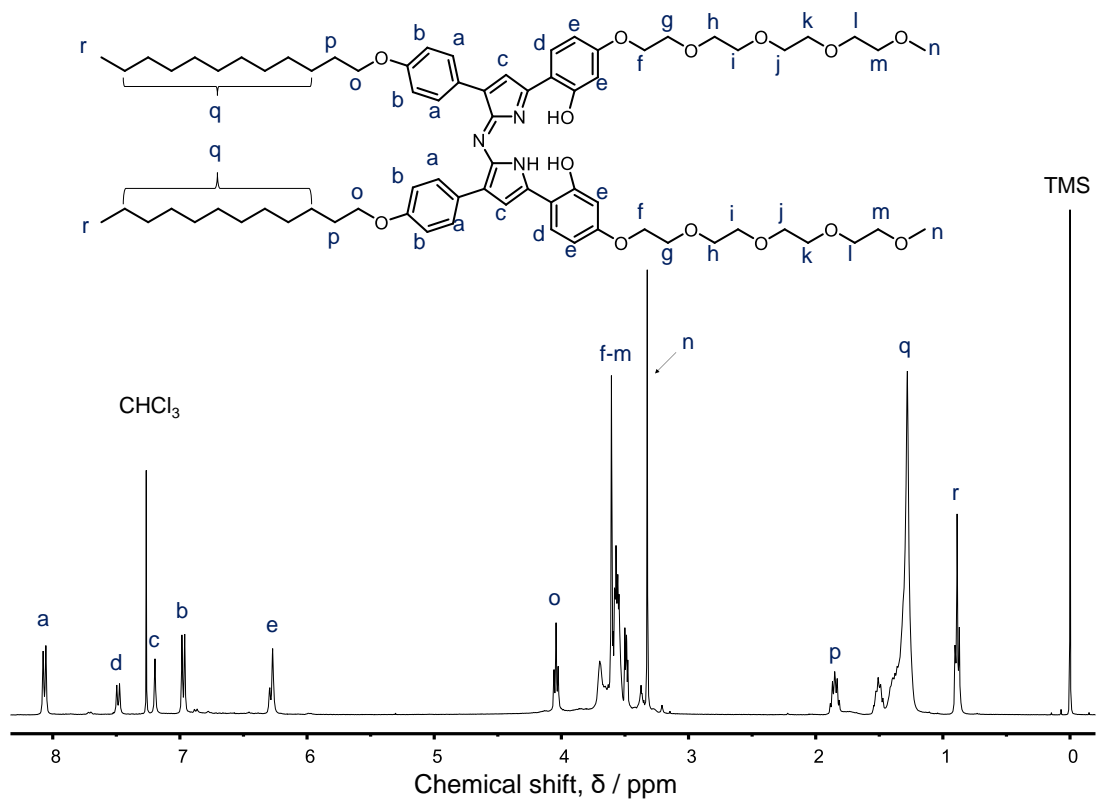


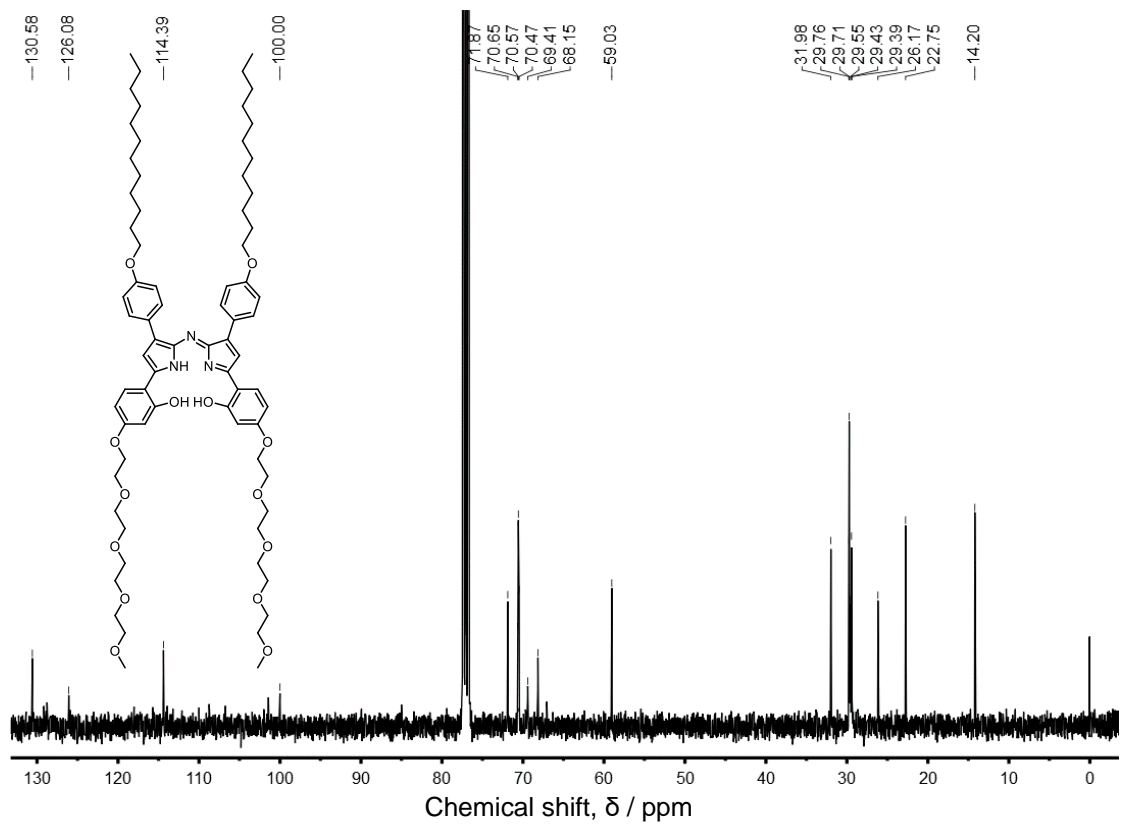


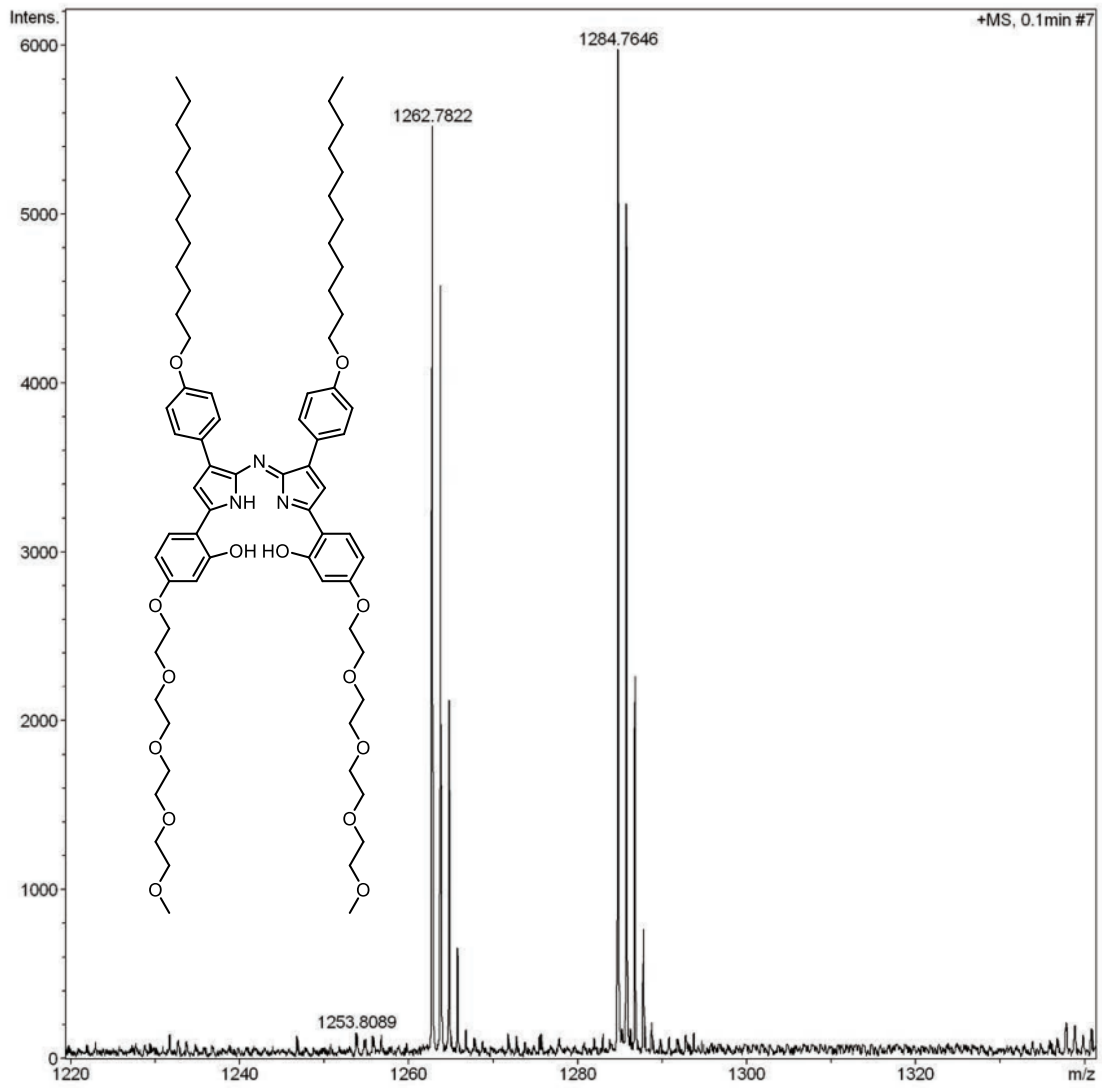


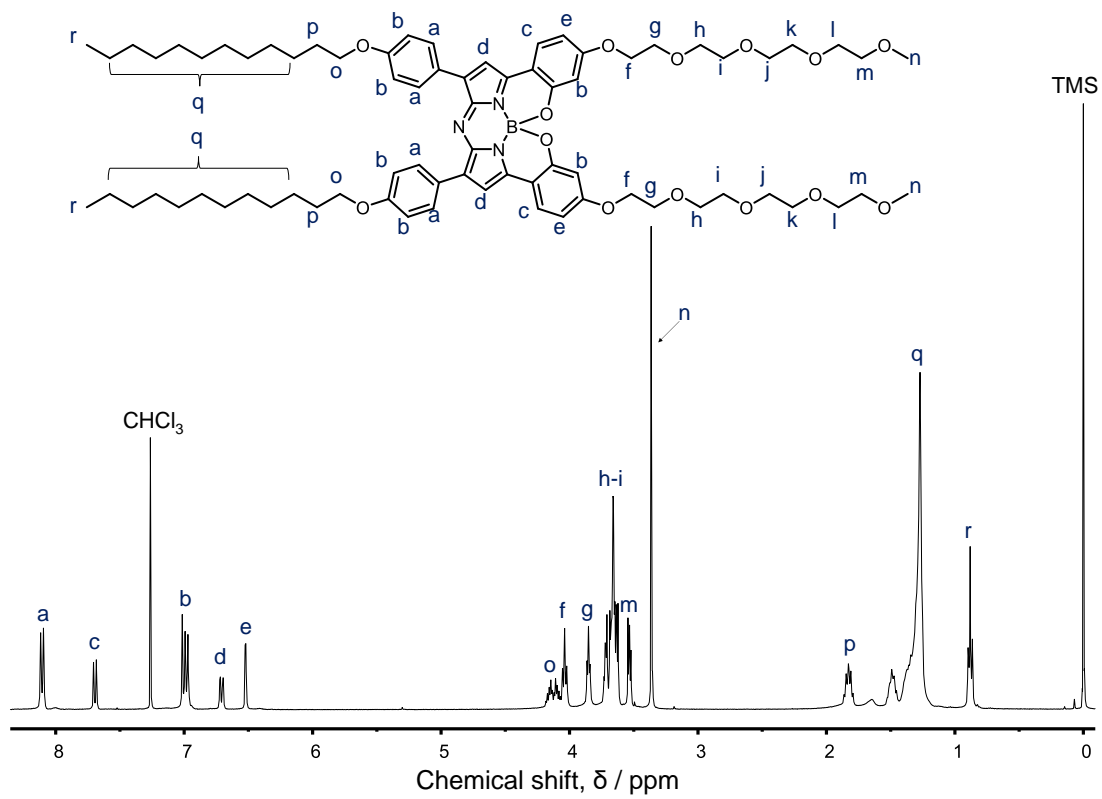


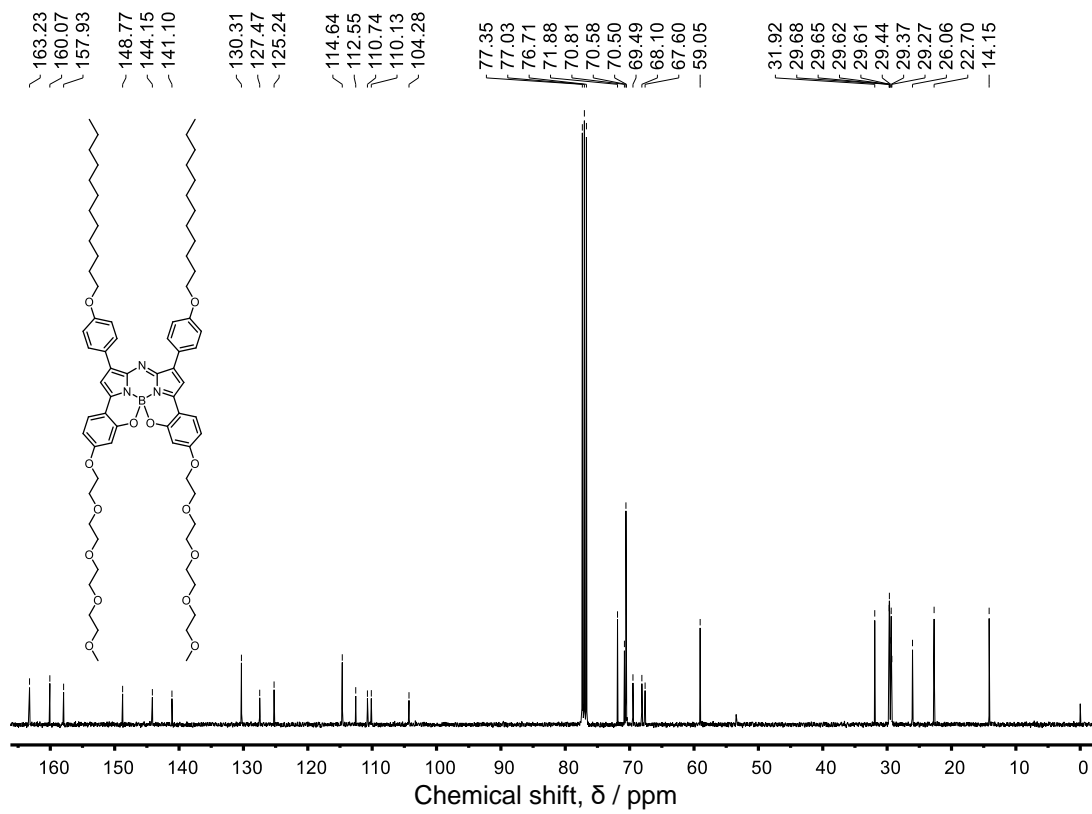




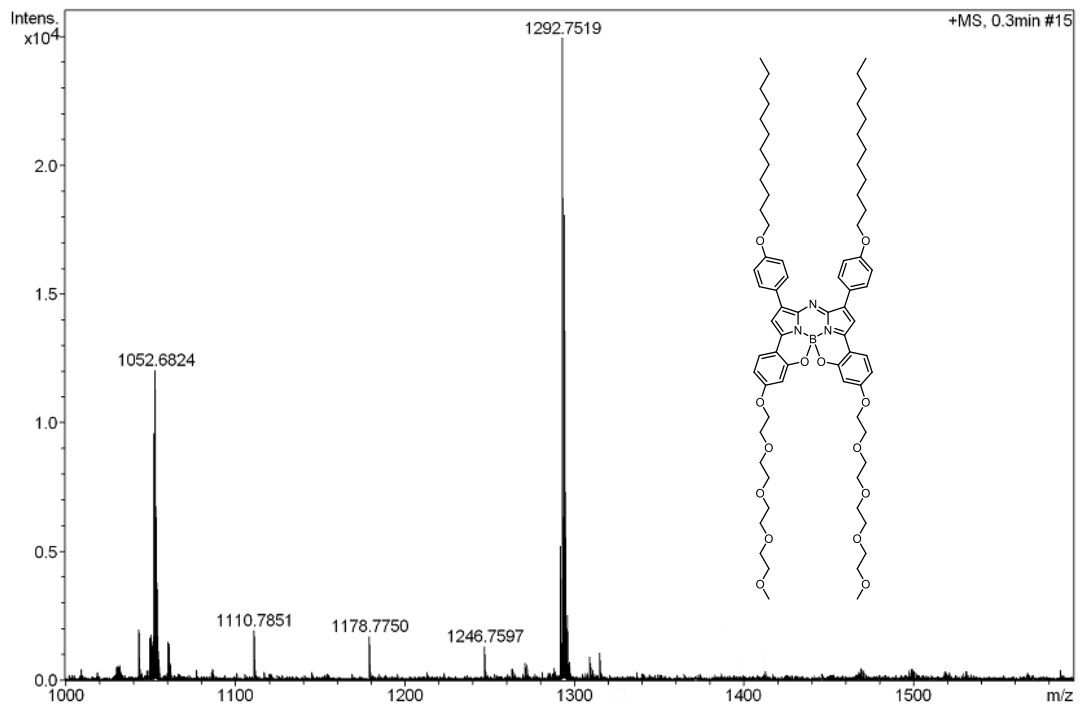




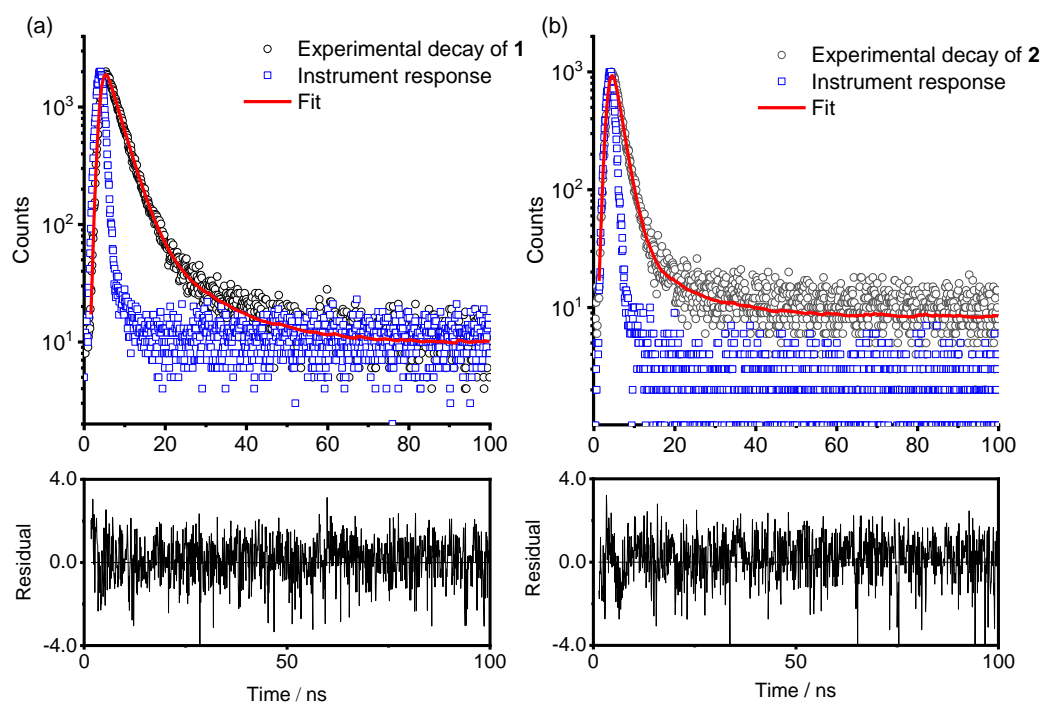




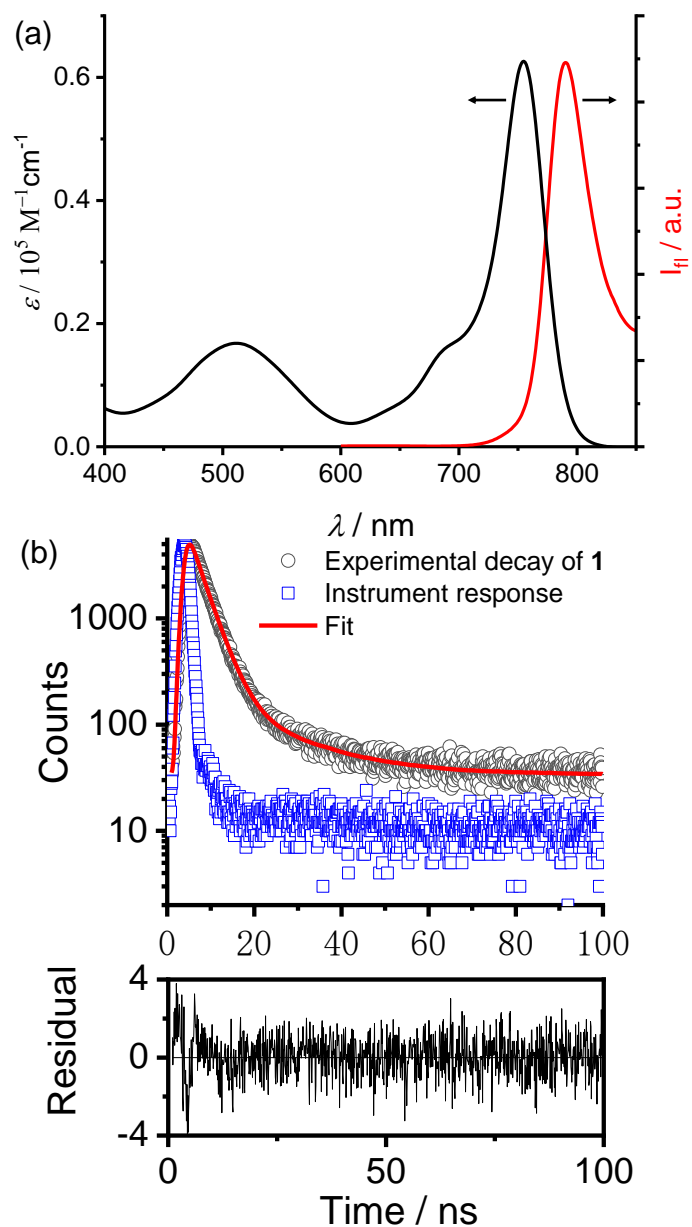




## 2. Vis/NIR absorption and fluorescence spectra of **1** and mass spectrum of $2 \cdot H^+$

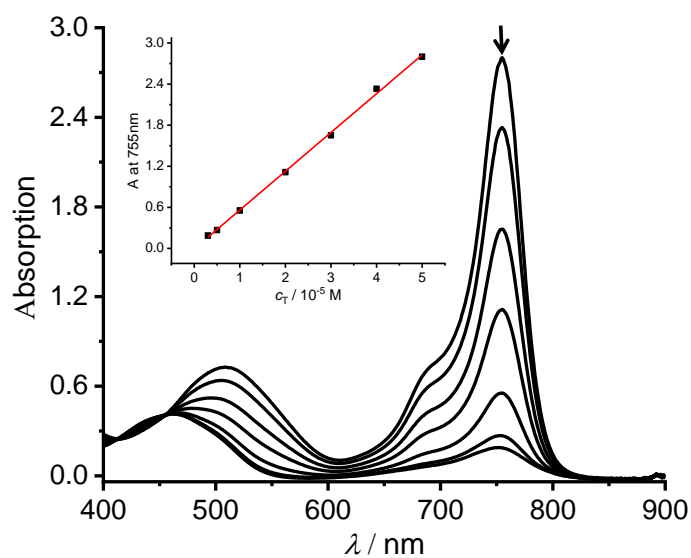


**Figure S1.** Fluorescence decay curves of dye **1** (a) in DMSO ( $\lambda_{\text{ex}} = 560$  nm) and dye **2** (b) in DMSO ( $\lambda_{\text{ex}} = 540$  nm).  $[1] = [2] = 5.0 \times 10^{-7}$  M.

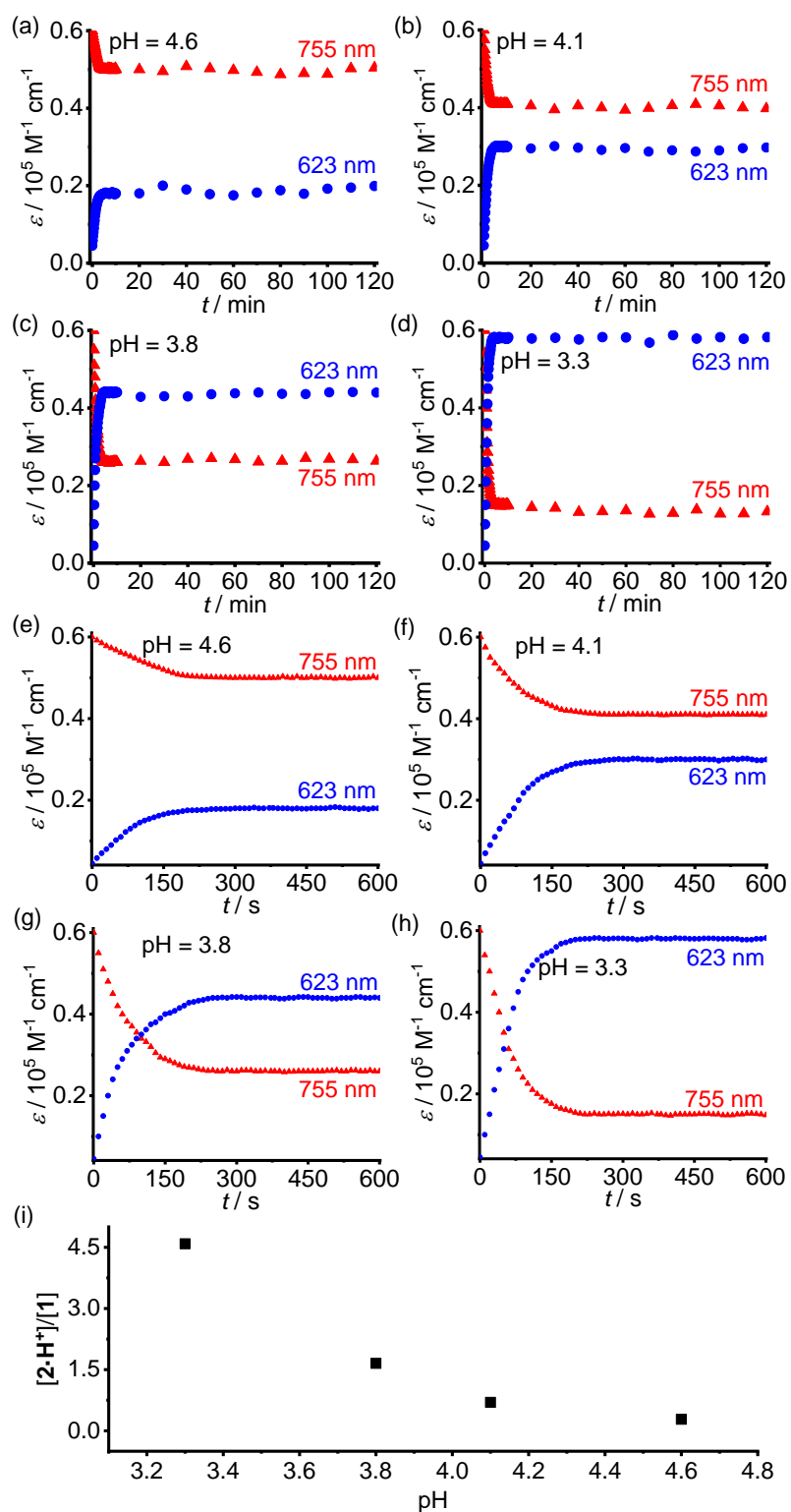


**Figure S2.** (a) Vis/NIR absorption and fluorescence spectra of **1** in CH<sub>3</sub>CN ( $c = 5.0 \times 10^{-7}$  M). (b) Fluorescence decay curve of dye **1** in CH<sub>3</sub>CN ( $\lambda_{\text{ex}} = 550$  nm). [**1**] =  $5.0 \times 10^{-7}$  M.

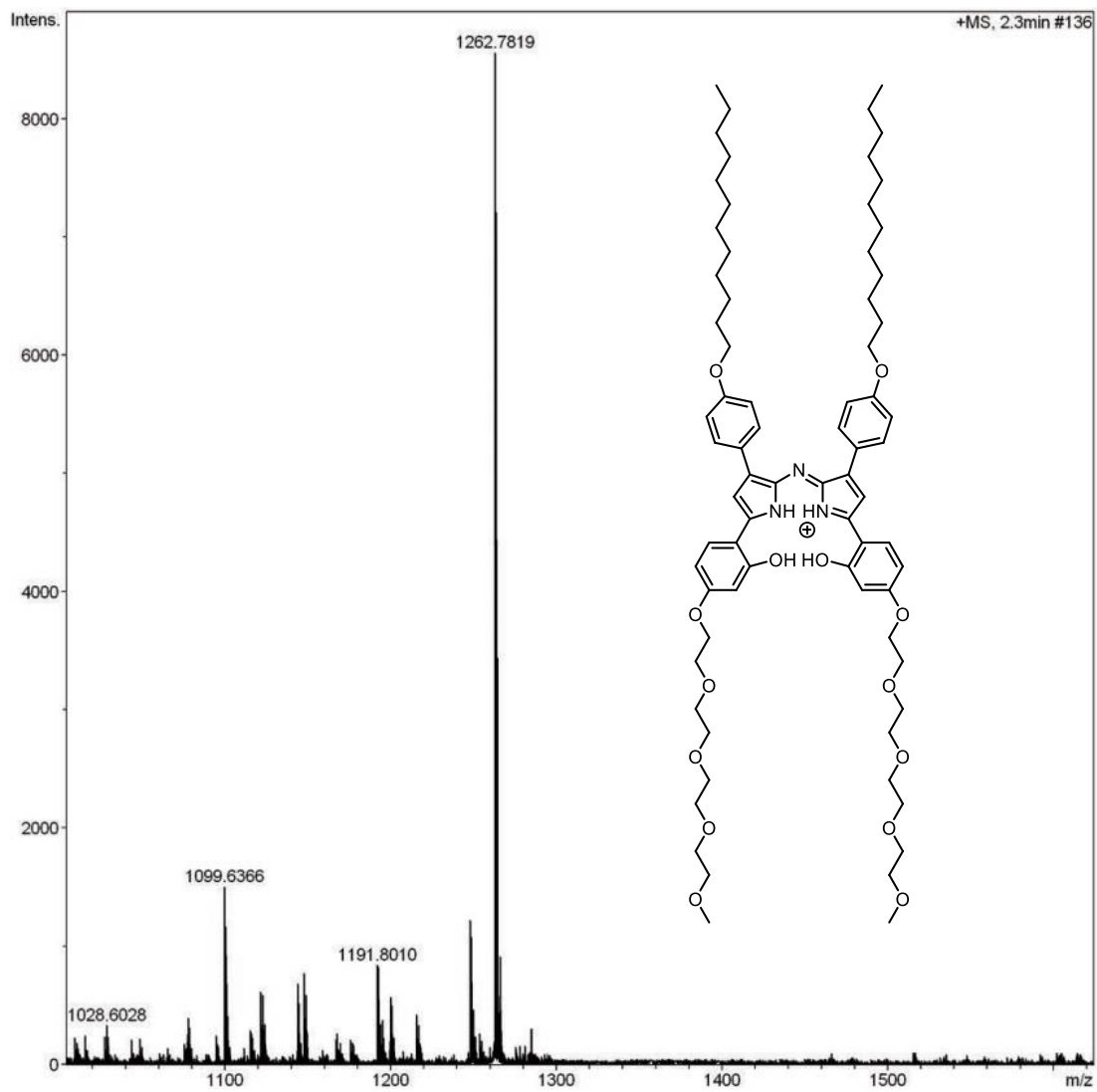
Acetonitrile was chosen as a suitable solvent for the pH-sensitivity experiment. According to concentration-dependent Vis/NIR spectra, the spectral change followed strictly the Lambert-Beer law and no aggregation was observed in the measured concentration range.



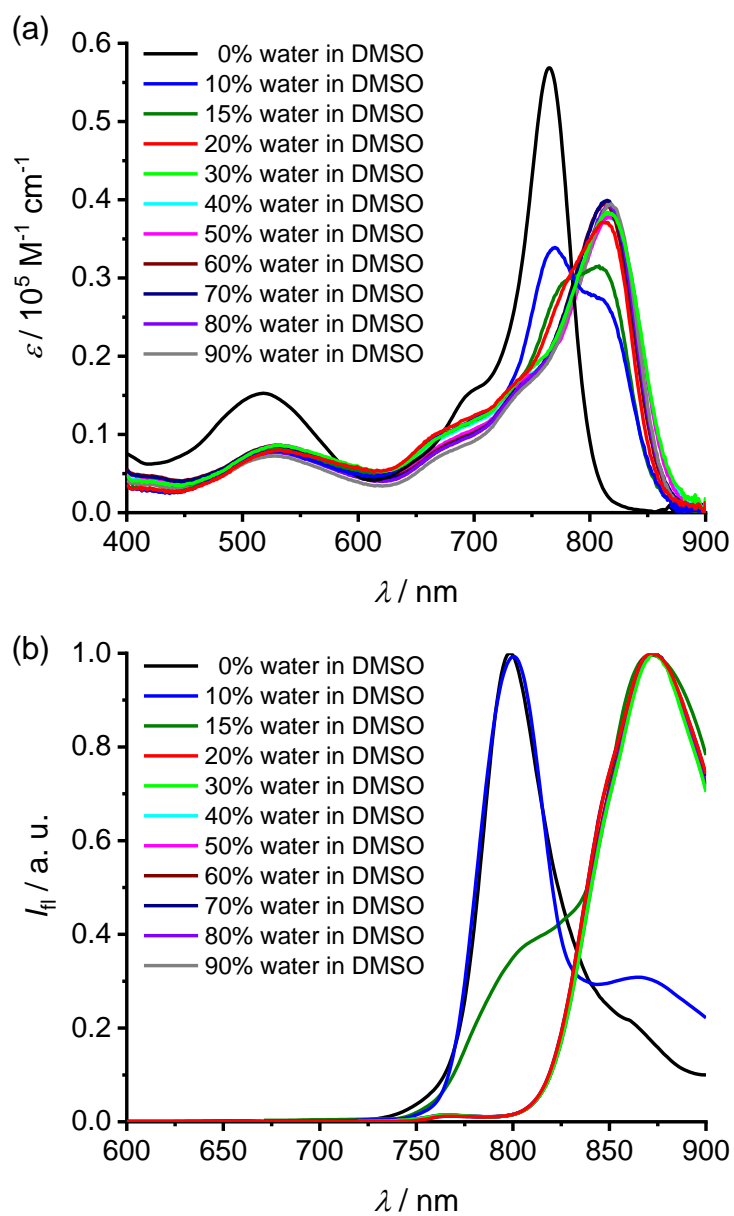
**Figure S3.** Concentration-dependent Vis/NIR spectra of **1** in CH<sub>3</sub>CN. The inset shows an excellent linear relationship between absorption at 755 nm and the total concentration  $c_T$ .



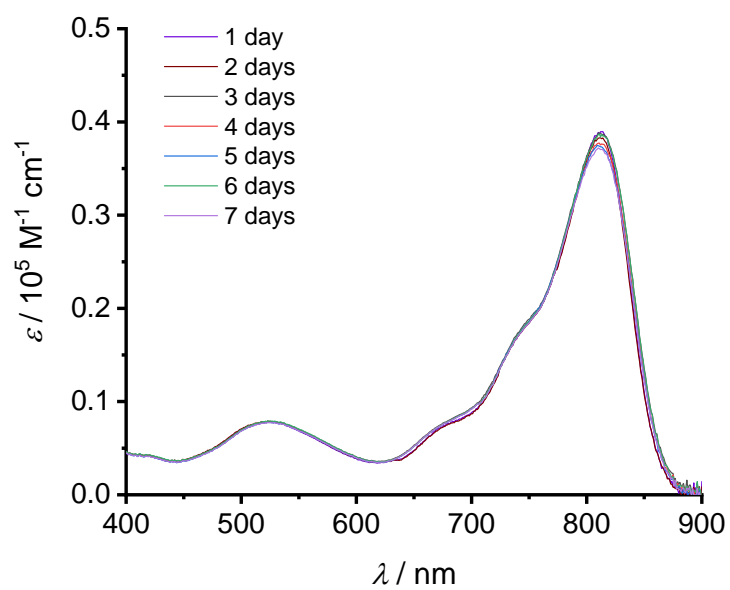
**Figure S4.** (a)-(d): Plots of  $\epsilon$  at 755 nm and 623 nm versus time (0-120 minutes) upon adding 10  $\mu\text{L}$  (a), 20  $\mu\text{L}$  (b), 35  $\mu\text{L}$  (c), 70  $\mu\text{L}$  (d) aqueous solution of TFA ( $[\text{TFA}] = 30 \text{ mM}$ ) into 3 mL solution of dye **1** in  $\text{CH}_3\text{CN}$  ( $[\text{1}] = 5.0 \times 10^{-5} \text{ M}$ ). (e-h) Local enlargement of changes of  $\epsilon$  versus time (0-10 min) for (a)-(d). (i) Plots of the calculated  $[2 \cdot \text{H}^+]/[1]$  in equilibrium state versus pH value of the solution.



**Figure S5.** High-resolution mass spectrum (ESI) for  $2 \cdot H^+$

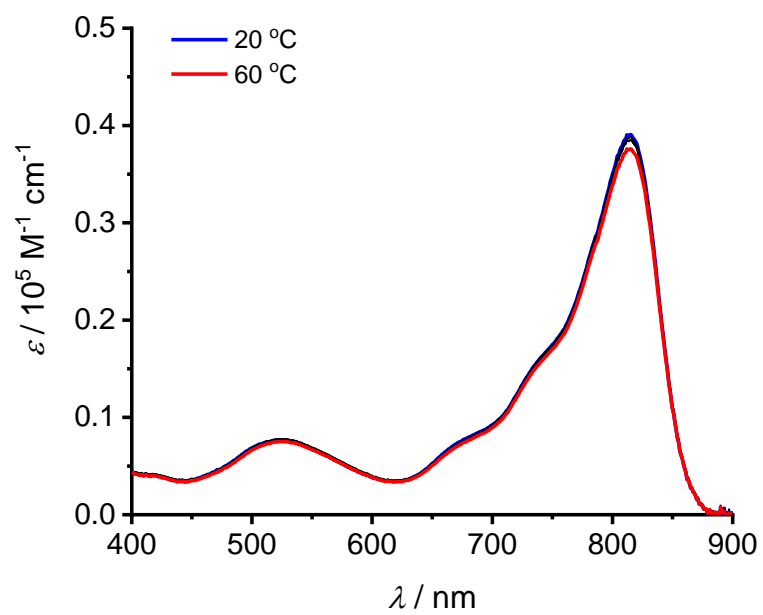


**Figure S6.** (a) Vis/NIR absorption and (b) emission spectra of **1** in DMSO with different portions of water at room temperature ( $c_T = 1.0 \times 10^{-6} \text{ M}$ ).



**Figure S7.** Time-dependent Vis/NIR absorption spectra of J-type aggregates of **1** at  $c_T = 5.0 \times 10^{-5} \text{ M H}_2\text{O/ DMSO}$  ( $v/v = 3/7$ ).





**Figure S8.** Temperature-dependent Vis/NIR absorption spectra of **1** in H<sub>2</sub>O/ DMSO ( $v/v = 3/7$ ) at  $c_T = 5.0 \times 10^{-5} \text{ M}$ .

### 3. Studies on thermodynamic aggregation properties and molecular packing

The molar fraction of aggregated molecules  $\alpha_{\text{agg}}$  at a certain temperature can be calculated based on the assumption that the dye molecules are in a fully assembled state ( $\alpha_{\text{agg}} = 1$ ) at lowest temperature ( $T = 295$  K) while they exist as monomers ( $\alpha_{\text{agg}} = 0$ ) at highest temperature ( $T = 333$  K). The absorption at a certain wavelength is considered to be the contribution of the monomers and aggregates as a whole (Eq. S1). Because the summation of the fractions of monomer and aggregated molecules equals unity (Eq. S2), the fraction of aggregated molecules can be calculated by solving the equations set of Eq. S1 and S2.

$$\varepsilon_T(766 \text{ nm}) = \varepsilon_{\text{mon}}\alpha_{\text{mon}} + \varepsilon_{\text{agg}}\alpha_{\text{agg}} \quad \text{S1}$$

$$\alpha_{\text{mon}} + \alpha_{\text{agg}} = 1 \quad \text{S2}$$

Temperature-dependent aggregation process can be fitted by the nucleation-elongation model proposed by Meijer et al.<sup>1</sup> The cooperative aggregation process can be described as two steps: nucleation and elongation.

In the elongation regime, the molar fraction of aggregates  $\alpha_{\text{agg}}$  can be estimated by Eq. S3, in which the  $\Delta H_e$  is the molar enthalpy release due to noncovalent interactions during elongation,  $T_e$  is the critical elongation temperature,  $\alpha_{\text{sat}}$  is a parameter introduced to ensure that  $\alpha_{\text{agg}}/\alpha_{\text{sat}}$  does not exceed unity.

$$\alpha_{\text{agg}} = \alpha_{\text{SAT}} \left( 1 - \exp \left[ \frac{-\Delta H_e}{RT_e^2} (T - T_e) \right] \right) \quad \text{S3}$$

At the temperature above  $T_e$  (nucleation regime), the fraction of aggregated molecules in the nucleation regime can be described as Eq. S4, where  $K_a$  is the dimensionless equilibrium constant of the activation step at  $T_e$ . The average length of the stack  $\langle N_n \rangle$  at  $T_e$  is given by Eq. S5.

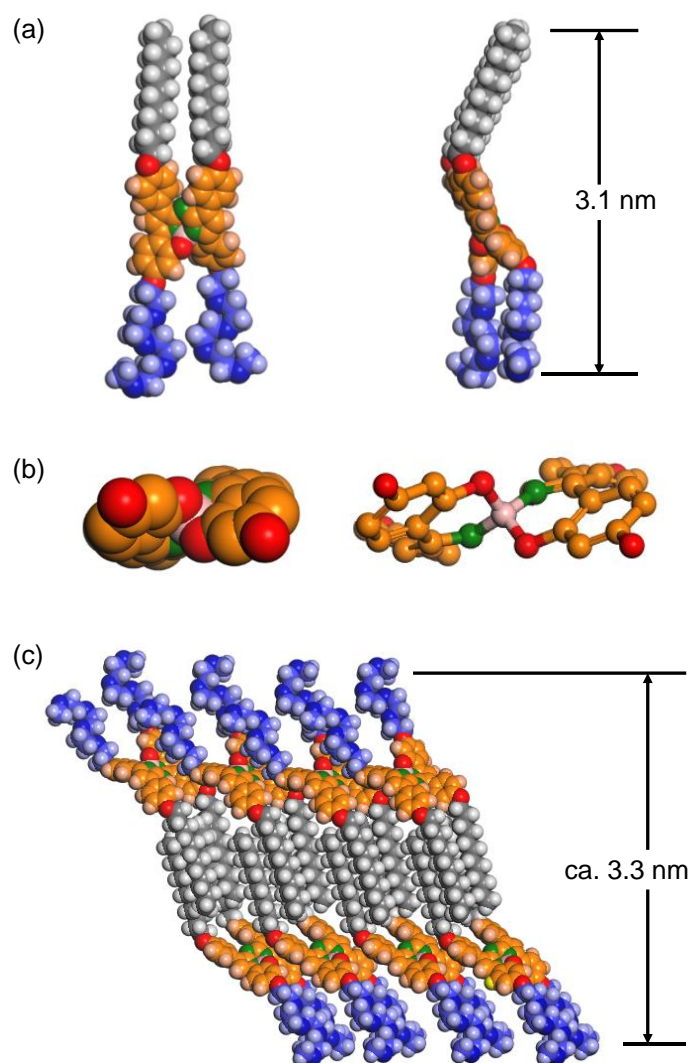
$$\alpha_{\text{agg}} = K_a^{1/3} \exp \left( \frac{2}{3} K_a^{-1/3} - 1 \right) \left[ \frac{\Delta H_e}{RT_e^2} (T - T_e) \right] \quad \text{S4}$$

$$\langle N_n(T_e) \rangle = \frac{1}{K_a^{1/3}} \quad \text{S5}$$

The thermodynamic parameters for the aggregation process of dye **1** at different concentrations (Table S1) can be obtained by fitting the above nucleation growth model with the temperature-dependent spectroscopic data of dye **1**.

**Table S1** Thermodynamic parameters of dye **1** including the elongation temperature ( $T_e$ ), molar enthalpy ( $\Delta H_e$ ), dimensionless equilibrium constant ( $K_a$ ) and the average length of the stack  $\langle N_n \rangle$  at  $T_e$ .

$c_T / 10^{-5} \text{ M}$	$T_e / ^\circ\text{C}$	$\Delta H_e / \text{kJ mol}^{-1}$	$K_a / 10^{-4}$	$\langle N_n \rangle$
3.0	45	-127.2	6.2	11.7
5.0	48	-130.6	7.3	11.1
8.0	50	-128.1	8.5	10.6
10.0	52	-134.4	14.0	8.9



**Figure S9.** (a) Front and side views of CPK model of dye **1**. (b) Chromophore viewed along the line from B atom to *meso*-N atom. (c) One proposed molecular stacking model of J-type aggregates of **1**. The aza-BODIPY chromophores, hydrophilic TEG chain and hydrophobic dodecyloxy groups of **1** are illustrated in orange, blue, and gray, respectively.

#### 4. Calculation of $pK_a$ for $2 \cdot H^+$

The molar fraction of dye **2** ( $\alpha_{\text{dye } 2}$ ) at a certain pH value can be calculated based on absorption spectra in Figure S10 by assuming that dye **2** is completely protonated to form  $2 \cdot H^+$  ( $\alpha_{\text{dye } 2} = 0$ ) at lowest pH (pH = 2.9) upon addition of 225  $\mu\text{L}$  TFA aqueous solution while no species of  $2 \cdot H^+$  exists in the system ( $\alpha_{\text{dye } 2} = 1$ ) at highest pH (pH = 7.0). The absorption at a certain wavelength is considered to be the collective contribution of dye **2** and  $2 \cdot H^+$  (Eq. S10). Because the summation of the fractions of **2** and  $2 \cdot H^+$  equals unity (Eq. S11), the fraction of **2** and  $2 \cdot H^+$  can be calculated by equations set of Eq. S10 and S11.

$$\varepsilon_{\text{pH}}(665 \text{ nm}) = \varepsilon_{\text{dye } 2} \alpha_{\text{dye } 2} + \varepsilon_{2 \cdot H^+} \alpha_{2 \cdot H^+} \quad \text{S10}$$

$$\alpha_{\text{dye } 2} + \alpha_{2 \cdot H^+} = 1 \quad \text{S11}$$

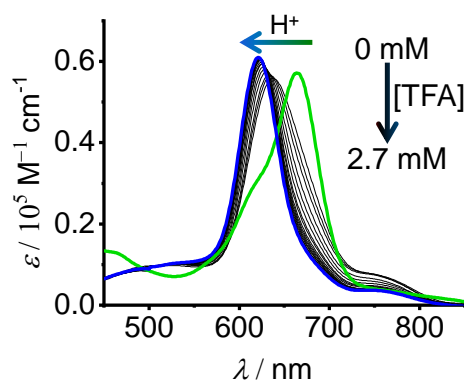
According to the absorption spectra (Figure S10) upon addition of 20  $\mu\text{L}$  aqueous TFA to 3 mL of **2** in  $\text{CH}_3\text{CN}$  (pH = 3.7),  $\alpha_{\text{dye } 2}$  is estimated to be 0.41. The  $pK_a$  of  $2 \cdot H^+$  is calculated to be 3.9 by using Eq. S12.

$$pK_a = \text{pH} - \lg \frac{\alpha_{\text{dye } 2}}{1 - \alpha_{\text{dye } 2}} \quad \text{S12}$$

Furthermore, the  $pK_a$  of  $2 \cdot H^+$  upon addition of various amount TFA were calculated and listed in Table S2. An averaged  $pK_a$  values of  $4.2 \pm 0.3$  was obtained for  $2 \cdot H^+$ .

**Table S2** The  $pK_a$  of  $2 \cdot H^+$  calculated based on absorption spectroscopic data upon addition of various amount TFA.

TFA / $\mu\text{L}$	5	15	25	35	45	55	65	75
pH	4.8	4.3	3.7	3.6	3.5	3.3	3.2	3.1
$pK_a$	4.7	4.4	3.9	3.9	4.0	4.1	4.2	4.1



**Figure S10.** Vis/NIR absorption spectra of **2** in  $\text{CH}_3\text{CN}$  ( $c = 5.0 \times 10^{-5} \text{ M}$ ) with increase in  $[\text{TFA}]$  from 0 mM to 2.7 mM.

## 5. References

- 1 (a) M. M. J. Smulders, A. P. H. J. Schenning and E. W. Meijer, *J. Am. Chem. Soc.*, 2008, **130**, 606-611; (b) P. Jonkheijm, P. van der Schoot, A. P. H. J. Schenning and E. W. Meijer, *Science*, 2006, **313**, 80-83.