# **Supplementary information**

## The enhancement of D-A effect of asymmetric Schiff Base by

## introducing acetyl group to diaminomalenitrile: synthesis,

## red fluorescence and crystal structure

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### I. Fluorescence Emission Spectra and relevant information

Fig. S20 Luminescence emission spectra ( $\lambda_{ex} = 420 \text{ nm}$ ) of L<sup>0</sup>. The concentration of L<sup>0</sup> is  $5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  at MeOH, EtOH, MeCN, THF, DMF, DMSO in a 1 cm cell. Fig. S21 Luminescence emission spectra ( $\lambda_{ex} = 475 \text{ nm}$ ) of L<sup>1</sup>. The concentration of L<sup>1</sup> is  $5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  at MeOH, EtOH, MeCN, THF, DMF, DMSO in a 1 cm cell. Fig. S22 Luminescence emission spectra ( $\lambda_{ex} = 420 \text{ nm}$ ) of Zn-L<sup>0</sup>. The concentration of Zn-L<sup>0</sup> is  $5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  at MeOH, EtOH, MeCN, THF, DMF, DMSO in a 1 cm cell.

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of **Zn-L**<sup>1</sup> is  $5.0 \times 10^{-5}$  mol·L<sup>-1</sup> at MeOH, EtOH, MeCN, THF, DMF, DMSO in a 1 cm cell.

#### **A. Experimental Section**

#### 1. Materials and instrumentation

All analytically reagents and solvents were obtained commercially and used without further purification. Diaminomaleonitrile, acetyl chloride, salicylaldehyde, and vanillic aldehyde were purchased from Ark.

Fourier transform infrared (FT-IR) spectra were measured on Thermo IS5 FT-IR spectrometer. <sup>1</sup>H NMR spectra were obtained using Bruker Ascend 400 MHz spectrometer with Si(CH<sub>3</sub>)<sub>4</sub> as an internal standard. Elemental (C, H, and N) analyses were carried out with a EA3000 elemental analyzer. Molecular simulations were carried out with the Gaussian 03 (revision E.03) program package. Equilibrium ground state geometry and electronic properties of the molecule was optimized by means of the density functional theory (DFT) method at the B3LYP level of theory with the 6-31 G(d) basic set. TU-1901 double-beam UV-Vis Spectrophotometer was used to measure UV-Vis absorption spectra. Fluorescence emission spectra for liquid state were recorded on Hitachi F-7000 fluorescence spectrophotometer at room temperature. Powder X-ray diffraction (PXRD) patterns were recorded on Bruker SMART APEX-CCD single-crystal diffractometer, German, using graphite monochromatic Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation. Thermogravimetric analyses (TGA) were carried out using a DTG-60H thermal analyzer under nitrogen atomosphere from room temperature to 800°C at the heating rate of 10°C /min.

#### 2. X-ray crystallography

Appropriate crystals of L<sup>1</sup>, Zn-L<sup>0</sup>, and Zn-L<sup>1</sup> were selected and measured on Bruker SMART APEX-CCD single-crystal diffractometer. Diffraction data were collected by  $\omega$ -2 $\theta$  scanning mode using graphite monochromatic Mo K $\alpha$  ( $\lambda = 0.71073$ Å) radiation at 153 K temperature and corrected by experience of absorption. Having been calculated by SHELXL crystallographic software, the crystal structures were analyzed and finished by the direct method. All hydrogen atoms were calculated by theoretical model and non-hydrogen atoms were refined on  $F^2$  by the full-matrix least-squares method.

#### 3. Synthesis of complexes

**Ac-DMN.** Acetyl chloride (1.000 g, 13.0 mmol) was dissolved by ethyl acetate (5 mL), this solution was transferred into constant pressure funnel, which was slowly added to diaminomaleonitrile (1.083 g, 10.0 mmol) dissolved by ethyl acetate (10 mL) under ice-water bath and stirring. Acetyl chloride with strong volatile ability and toxicity must be measured in fuming cupboard with completed protection. The color of product was turning brown to claybank. By means of suction filtrating and washing with ethyl acetate (10 mL), yellow powder was got. Then transferred powder to beaker and dissolved that with deionized water (8 mL) under stirring for 0.5 h. Added by anhydrous ether (8 mL) to beaker, the flocculent appeared. The complex (Ac-DMN) was obtained after suction filtrating, washing with anhydrous ether (5 mL), and drying at 40°C. Yield: 0.941 g (6.26 mmol, 62.6%). Anal. Calcd for Ac-DMN [C<sub>6</sub>H<sub>6</sub>ON<sub>4</sub> (150.14)]: C, 48.00; H, 4.03; N, 37.32. Found: C, 48.23; H, 4.09; N, 37.29. <sup>1</sup>H NMR ( $d_6$ -DMSO, 400 MHz, ppm): 9.14 (s, 1H), 7.20 (s, 2H), 1.94 (s, 3H).

**L**<sup>0</sup>. Weighed in beaker and dissolved by ethyl alcohol (5 mL) under stirring, Ac-DMN (1.501 g, 10.0 mmol) was added to salicylaldehyde (1.220 g, 10.0 mmol) dissolved by ethyl alcohol (10 mL) with a drop of concentrated hydrochloric acid. The mixture was refluxing for 8 h at 80°C. After cooling and suction filtrating, yellow powder **L**<sup>0</sup> washed by ethyl alcohol (10 mL) and anhydrous ether (10 mL) was obtained. Drying at 60°C **L**<sup>0</sup> was received. Yield: 1.850 g (7.28 mmol, 72.8%). Anal. Calcd (%) for **L**<sup>0</sup> [C<sub>13</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub> (254.25)]: C, 61.41; H, 3.96; N, 22.04. Found: C, 61.40; H, 3.94; N, 22.00. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz, ppm): 10.76 (s, 2H), 8.9 (s, 1H), 8.23-8.22 (d, 1H), 7.47-7.45 (d, 1H), 7.00-6.96 (dd, 2H), 2.21 (s, 3H). <sup>13</sup>C NMR (DMSO- *d*<sub>6</sub>, 125 MHz, δ, ppm): 112.72, 114.16, 115.92, 117.37, 120.20, 121.34, 130.26, 136.06, 160.16, 168.77. MS (EI, m/z): 255.0868 ([M]+, calcd for C<sub>13</sub>H<sub>10</sub>N4O<sub>2</sub>, 254.25).

L<sup>1</sup>. Synthesis of L<sup>1</sup> was similar to L<sup>0</sup>, except for that vanillic aldehyde was changed to 4-(diethylamino)salicylaldehyde and finally powder was orange. Yield: 2.585 g (7.94 mmol, 79.46%). <sup>1</sup>H NMR ( $d_6$ -DMSO, 400 MHz, ppm): 1.14 (t, *J*=7.0 Hz, 6H), 2.13 (s, 3H), 3.51-3.37 (m, 4H), 6.13 (d, *J*=2.5 Hz, 1H), 6.40 (dd, *J*=9.2, 2.3 Hz, 1H), 7.81 (d,

*J*=8.9 Hz, 1H), 8.58 (s, 1H), 10.46(s, 1H), 10.88(s, 1H). The crystal of  $L^1$  was got by evaporating mixture that  $L^1$  dissolved in methyl alcohol (3 mL) and acetonitrile (3 mL) at room temperature for 5 days. Anal. Calcd (%) for  $L^1$  [C<sub>17</sub>H<sub>19</sub>N<sub>5</sub>O<sub>2</sub>·CH<sub>3</sub>CN (366.43)]: C, 62.27; H, 6.05; N, 22.92. Found: C, 61.99; H, 5.99; N, 22.97.

**Zn-L<sup>0</sup>. Zn-L<sup>0</sup>** was synthesized by dissolving **L**<sup>0</sup> (0.013 g, 0.05 mmol) and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.014 g, 0.05 mmol) in solvent respectively which mixed with methyl alcohol (3 mL) and acetonitrile (3 mL). A drop of triethylamine was added to the solution of **L**<sup>0</sup>. Under stirring for 0.5 h, two liquids were blended, then continue to stir for 0.5 h. The mixture was filtered and the single crystal of **Zn-L**<sup>0</sup> was obtained by evaporation at room temperature after 7 days. Anal. Calcd (%) for **Zn-L**<sup>0</sup> [C<sub>27</sub>H<sub>22</sub>N<sub>8</sub>O<sub>6</sub>Zn<sub>2</sub> (685.31)]: C, 47.32; H, 3.24; N, 16.35. Found: C, 47.36; H, 3.21; N, 16.32.

**Zn-L<sup>1</sup>. Zn-L<sup>1</sup>** was obtained as the same as **Zn-L<sup>0</sup>**, but the ligand was different. Anal. Calcd (%) for **Zn-L<sup>1</sup>** [C<sub>57</sub>H<sub>68</sub>N<sub>16</sub>O<sub>8</sub>Zn<sub>3</sub> (1301.38)]: C, 52.61; H, 5.27; N, 17.22. Found: C, 52.65; H, 5.30; N, 17.19.

## **B.** Thermogravimetric Analysis



**Fig. S1** TG curves of two ligands  $L^0$  and  $L^1$  at the heating rate of 10°C/min. The curves showed the weight loss process. The residue of complexes was beginning to decompose around 263-278°C (263°C for  $L^0$ , 278°C for  $L^1$ ).



**Fig. S2** TG curves of two ligands **Zn-L<sup>0</sup>** and **Zn-L<sup>1</sup>** at the heating rate of 10°C/min. The curves showed the weight loss process. The **Zn-L<sup>0</sup>** initial weight loss (obs. 6.9%, cal. 7.3%) in the temperature range 270–390°C is assigned to the loss of coordinated solvates molecules per formula unit. The residue of complexes was beginning to decompose around 427°C. The **Zn-L<sup>1</sup>** initial weight loss (obs. 9.2%, cal. 9.8%;) in the temperature range 180–220°C is assigned to the loss of protonated triethylamine and water molecules per formula unit. The residue of complexes was beginning to decompose around 310°C.

## C. PXRD spectra



Fig. S3 PXRD patterns for the simulated and experimental  $L^1$  soaked in water and aqueous solutions with pH ranging from 2 to 10 for one day.

## **D. DFT Study**

**Table S1** Primary orbitals which contribute to the calculated transitions of  $L^0$  (iso = 0.03).

							×, ∖
LUMO	-3.01 eV	НОМО	-6.41 eV	HOMO-1	-6.96 eV	HOMO-2	-7.71 eV

**Table S2** Primary orbitals which contribute to the calculated transitions of  $L^1$  (iso = 0.03).

LUMO+1	-1.42 eV	LUMO	-2.83 eV	номо	-5.96 eV	HOMO-1	-6.50 eV
НОМО-2	-6.91 eV						

## **E. Bonding Constants**



Fig. S4 The Benesi-Hilderbrand curve of  $L^0$  for zinc.



**Fig. S5** The Benesi-Hilderbrand curve of  $L^1$  for zinc.

Complex	$\mathbf{L}^{1}$	Zn-L <sup>0</sup>	$Zn-L^1$
Formula	$C_{19}H_{22}N_6O_2$	$C_{27}H_{22}N_8O_6Zn_2$	$C_{57}H_{68}N_{16}O_8Zn_3$
Mr	366.43	685.31	1301.38
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1$	$P2_{1}2_{1}2$	$P\overline{1}$
<i>a</i> (Å)	4.7990(17)	17.578(11)	12.456(2)
<i>b</i> (Å)	16.672(6)	8.180(5)	13.244(2)
<i>c</i> (Å)	12.400(4)	10.632(7)	19.423(3)
α (°)	90	90	90.368(5)
eta (°)	89.940(2)	90	96.639(5)
γ (°)	90	90	101.761(5)
$V(Å^3)$	992.2(6)	1528.8(17)	3114.3(9)
Ζ	2	4	2
F(000)	388.0	696	1352
Reflections used	2159	3549	2192
Independent reflections	3778	2699	11379
Goodness-of-fit on $F^2$	1.023	1.019	1.020
$R_{\rm int}$	0.0697	0.0724	0.0598
$R_1[I > 2\sigma(I)]$	0.0876	0.0476	0.0571
$wR_2[I > 2\sigma(I)]$	0.2112	0.1216	0.1427
$R_1(\text{all data})$	0.1276	0.0641	0.1054
$wR_2(all data)$	0.2319	0.1282	0.1662

## F. Crystallographic Data and Crystal Structure

O(1)–C(2)	1.207(7)	C(7)–C(8)	1.418(8)
N(4)–C(7)	1.314(7)	N(4)–C(5)	1.393(8)
C(8)–C(13)	1.406(9)	N(1)–C(2)	1.375(8)
N(1)–C(3)	1.378(8)	C(16)–C(17)	1.480(19)
C(9)–C(10)	1.363(9)	C(9)–O(2)	1.366(7)
C(9)–C(8)	1.398(8)	N(2)–C(4)	1.144(9)
C(2)–C(1)	1.482(10)	N(5)–C(11)	1.381(9)
N(5)–C(14)	1.464(11)	N(5)–C(16)	1.491(12)
C(14)–C(15)	1.484(13)	N(3)–C(6)	1.135(9)
C(10)–C(11)	1.403(9)	C(5)–C(3)	1.352(8)
C(5)–C(6)	1.428(10)	C(4)–C(3)	1.439(9)
C(18)–C(19)	1.47(2)	C(12)–C(13)	1.360(9)
C(12)–C(11)	1.407(10)	N(6)–C(19)	1.08(2)
C(7)–N(4)–C(5)	120.4(5)	C(10)-C(11)-C(12)	117.8(5)
C(2)–N(1)–C(3)	123.1(5)	C(5)–C(3)–N(1)	122.5(5)
C(5)-C(3)-C(4)	119.8(5)	N(1)-C(3)-C(4)	117.5(5)
C(10)–C(9)–O(2)	118.0(5)	C(17)–C(16)–N(5)	112.7(9)
C(10)–C(9)–C(8)	121.8(5)	O(2)–C(9)–C(8)	120.2(5)
O(1)–C(2)–N(1)	121.6(6)	O(1)–C(2)–C(1)	123.4(6)
N(1)-C(2)-C(1)	114.9(6)	C(11)-N(5)-C(14)	120.3(7)
C(11)–N(5)–C(16)	120.7(7)	C(14)-N(5)-C(16)	118.9(7)
C(9)–C(10)–C(11)	121.4(6)	C(3)–C(5)–N(4)	120.8(5)
C(3)–C(5)–C(6)	118.9(6)	N(4)-C(5)-C(6)	120.4(6)
N(2)-C(4)-C(3)	177.4(7)	N(3)–C(6)–C(5)	177.0(7)
C(13)-C(12)-C(11)	119.6(6)	N(5)-C(14)-C(15)	114.3(8)
N(4)–C(7)–C(8)	123.3(5)	C(9)–C(8)–C(13)	115.9(5)
C(9)–C(8)–C(7)	123.6(5)	C(13)–C(8)–C(7)	120.5(6)
C(12)–C(13)–C(8)	123.4(6)	N(5)-C(11)-C(10)	121.2(6)
N(5)–C(11)–C(12)	121.0(6)		

Table S4 Selected bond distances (Å) and angles (°) for  $L^1$ .

Zn(1)–O(1)	2.017(6)	Zn(1)–O(2)	2.033(6)
Zn(1)-N(1)	2.069(6)	Zn(1)-O(3)#1	1.996(6)
Zn(1)–N(2)	2.136(6)		
O(3)–Zn(1)–O(1)#1	94.8(2)	O(2)–Zn(1)–N(2)	95.8(3)
O(3)–Zn(1)–O(2)#1	105.0(3)	N(1)–Zn(1)–N(2)	79.4(2)
O(1)–Zn(1)–O(2)	90.0(2)	O(2)–Zn(1)–N(1)	125.4(3)
O(3)–Zn(1)–N(1)	129.6(2)	O(3)–Zn(1)–N(2)#1	94.6(2)
O(1)–Zn(1)–N(1)	88.0(2)	O(1)–Zn(1)–N(2)	167.3(2)

Table S5 Selected bond distances (Å) and angles (°) for Zn-L<sup>0</sup>.

Symmetry transformations used to generate equivalent atoms: (#1) -x + 1/2, y + 1/2, -z.

Table 50 Selected bolid distances (A) and angles () for Zh-L.						
O(10)–Zn(3)	2.068(3)	Zn(2)–O(30)	2.008(3)			
O(10)–Zn(2)	2.076(3)	Zn(2)–N(21)	2.075(4)			
O(10)–Zn(1)	2.079(3)	Zn(2)–N(3)	2.075(4)			
Zn(3)–O(3)	1.984(3)	Zn(1)–O(1)	1.983(3)			
Zn(3)–O(1)	2.122(3)	Zn(1)–O(30)	2.116(3)			
Zn(3)–N(20)	2.081(4)	Zn(1)–N(17)	2.080(4)			
Zn(3)–N(7)	2.075(4)	Zn(1)–N(10)	2.069(5)			
Zn(2)–O(3)	2.130(3)					
Zn(3)–O(10)–Zn(2)	99.4(1)	O(1)–Zn(1)–O(10)	82.4(1)			
Zn(3)–O(10)–Zn(1)	98.4(1)	O(1)–Zn(1)–O(30)	96.9(1)			
Zn(2)–O(10)–Zn(1)	99.4(1)	O(1)–Zn(1)–N(17)	124.4(1)			
O(10)–Zn(3)–O(1)	79.4(1)	O(1)–Zn(1)–N(10)	104.6(2)			
O(10)–Zn(3)–N(20)	144.9(2)	N(17)-Zn(1)-O(30)	83.4(2)			
O(10)–Zn(3)–N(7)	107.9(1)	N(10)-Zn(1)-O(10)	108.3(2)			
O(3)–Zn(3)–O(10)	81.8(1)	N(10)-Zn(1)-O(30)	158.0(2)			
O(3)–Zn(3)–O(1)	94.6(1)	N(10)-Zn(1)-N(17)	80.7(2)			
O(3)–Zn(3)–N(20)	129.4(1)	Zn(3)–O(3)–Zn(2)	100.4(11)			
O(3)–Zn(3)–N(7)	106.4(2)	C(11)–O(3)–Zn(3)	126.9(3)			
N(20)–Zn(3)–O(1)	82.1(1)	C(11)–O(3)–Zn(2)	132.0(3)			
N(7)–Zn(3)–O(1)	158.5(1)	Zn(1)–O(1)–Zn(3)	99.8(1)			
N(7)-Zn(3)-N(20)	80.8(1)	C(30)–O(1)–Zn(3)	131.1(3)			
O(10)–Zn(2)–O(3)	78.3(1)	C(30)–O(1)–Zn(1)	129.1(3)			
O(30)–Zn(2)–O(10)	81.4(1)	Zn(2)–O(30)–Zn(1)	100.4(1)			
O(30)–Zn(2)–O(3)	95.8(1)	C(1)–O(30)–Zn(2)	128.2(3)			
O(30)–Zn(2)–N(21)	127.8(1)	C(1)–O(30)–Zn(1)	131.4(3)			
O(30)–Zn(2)–N(3)	103.2(2)	C(29)–N(20)–Zn(3)	128.3(3)			
N(21)-Zn(2)-O(10)	146.9(1)	C(42)-N(20)-Zn(3)	111.0(3)			
N(21)–Zn(2)–O(3)	82.9(1)	C(26)–N(21)–Zn(2)	129.5(3)			
N(21)–Zn(2)–N(3)	80.9(2)	C(21)–N(21)–Zn(2)	110.3(3)			
N(3)–Zn(2)–O(10)	110.0(1)	C(27)–N(17)–Zn(1)	127.9(4)			
N(3)–Zn(2)–O(3)	160.2(2)	C(91)–N(17)–Zn(1)	111.3(4)			
O(10)–Zn(1)–O(30)	78.9(1)	C(41)–N(7)–Zn(3)	110.5(3)			
O(10)–Zn(1)–N(17)	149.6(2)	C(39)–N(7)–Zn(3)	131.2(3)			
C(20)–N(3)–Zn(2)	110.7(3)	C(90)–N(10)–Zn(1)	110.9(4)			
C(24)–N(3)–Zn(2)	130.0(4)	C(54)–N(10)–Zn(1)	130.3(5)			

Table S6 Selected bond distances (Å) and angles (°) for Zn-L<sup>1</sup>.



Fig. S6 Coordinated modes of (a) Zn-L<sup>0</sup>; (b) Zn-L<sup>1</sup>.



Fig. S7 The trinuclear structure of  $Zn-L^1$  with containing free protonated triethylamine and water.

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**Fig. S8** The 3D structure of **Zn-L**<sup>1</sup> containing free protonated triethylamine and water from a axis.



**Fig. S9** The 3D structure of  $\mathbf{Zn-L^0}$  from *a* axis.



**Fig. S10** The 3D structure of  $\mathbf{Zn}$ - $\mathbf{L}^{0}$  from *b* axis.



**Fig. S11** The 3D structure of **Zn-L<sup>0</sup>** from *c* axis. The distance of two adjacent –CN are 13.4146 Å.



**Fig. S12** The 3D structure of  $\mathbf{Zn}$ - $\mathbf{L}^1$  from *a* axis.



**Fig. S13** The 3D structure of  $\mathbf{Zn}$ - $\mathbf{L}^1$  from c axis.

## G. IR Spectra



Fig. S14 IR spectra of L<sup>0</sup> and Zn-L<sup>0</sup>.



Fig. S15 IR spectra of  $L^1$  and  $Zn-L^1$ .

### H. UV/vis Spectra



Fig. S16 UV/vis absorption spectra of  $L^0$  in aqueous solution. The spectra were obtained by measuring  $5.0 \times 10^{-5}$  mol·L<sup>-1</sup> solution at MeOH, EtOH, MeCN, THF, DMF, DMSO in a 1 cm cell.



Fig. S17 UV/vis absorption spectra of  $L^1$  in aqueous solution. The spectra were obtained by measuring  $5.0 \times 10^{-5}$  mol·L<sup>-1</sup> solution at MeOH, EtOH, MeCN, THF, DMF, DMSO in a 1 cm cell.



Fig. S18 UV/vis absorption spectra of  $Zn-L^0$  in aqueous solution. The spectra were obtained by measuring  $5.0 \times 10^{-5}$  mol·L<sup>-1</sup> solution at MeOH, EtOH, MeCN, THF, DMF, DMSO in a 1 cm cell.



Fig. S19 UV/vis absorption spectra of  $Zn-L^1$  in aqueous solution. The spectra were obtained by measuring  $5.0 \times 10^{-5}$  mol·L<sup>-1</sup> solution at MeOH, EtOH, MeCN, THF, DMF, DMSO in a 1 cm cell.

### I. Fluorescence Emission Spectra and relevant information



Fig. S20 Luminescence emission spectra ( $\lambda_{ex} = 420 \text{ nm}$ ) of L<sup>0</sup>. The concentration of L<sup>0</sup> is  $5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  at MeOH, EtOH, MeCN, THF, DMF, DMSO in a 1 cm cell.



Fig. S21 Luminescence emission spectra ( $\lambda_{ex} = 475$  nm) of L<sup>1</sup>. The concentration of L<sup>1</sup> is  $5.0 \times 10^{-5}$  mol·L<sup>-1</sup> at MeOH, EtOH, MeCN, THF, DMF, DMSO in a 1 cm cell.



**Fig. S22** Luminescence emission spectra ( $\lambda_{ex} = 420 \text{ nm}$ ) of **Zn-L<sup>0</sup>**. The concentration of **Zn-L<sup>0</sup>** is  $5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  at MeOH, EtOH, MeCN, THF, DMF, DMSO in a 1 cm cell.



Fig. S23 Luminescence emission spectra ( $\lambda_{ex} = 475 \text{ nm}$ ) of Zn-L<sup>1</sup>. The concentration of Zn-L<sup>1</sup> is  $5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  at MeOH, EtOH, MeCN, THF, DMF, DMSO in a 1 cm cell.