Electronic Supplementary Information for

A Highly Sensitive Viscosity Probe Based on Ferrocene-BODIPY Dyads

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§1. Measurements and Materials

The ^{1}H-NMR , ^{13}C-NMR spectra were recorded on a BRUCK 400MHz instrument and the TOF-MS spectra were determined using a BEFLEX III. Elemental analyses were performed on a Carlo-Erba-1106 instrument.

The UV-Visible absorption spectra were measured with a Shimadzu UV-1601PC double-beam spectrophotometer. The steady-state fluorescence measurements were carried out with a Hitachi F-4500 Fluorospectrometer, using a Xe lamp as the excitation source with a 1 cm quartz cell.

Cyclic voltammograms (CVs) were recorded on a CHI660B electrochemical workstation (CH Instruments, Austin, TX). The working electrode consisted of a glassy carbon disk (3.0 mm in diameter) that was polished on a felt pad with 0.05μm alumina (Buehler, Ltd., Lake Bluff, IL), sonicated in water and absolute ethanol for 3 min, and then dried in a oven at 100°C before being transferred into the inert atmosphere dry box. A platinum wire served as a counter electrode, and a silver wire was utilized as a quasi-reference electrode which was referenced after each series of experiments against the ferrocene/ferrocenium couple to obtain the potentials vs SCE,[1] taking $E°(\mathrm{Fc/Fc+})=0.424$ V, vs SCE.[2] The concentrations used to obtain each voltammogram are given in the corresponding figure captions.

The fluorescence quantum yields (Φ_F) of **FcEB** were calculated by the steady-state comparative method using the following equation[3] with 4-iodophenyl-BODIPY as standard material ($\Phi_{st} = 0.64$, $CHCl_3$). [4]

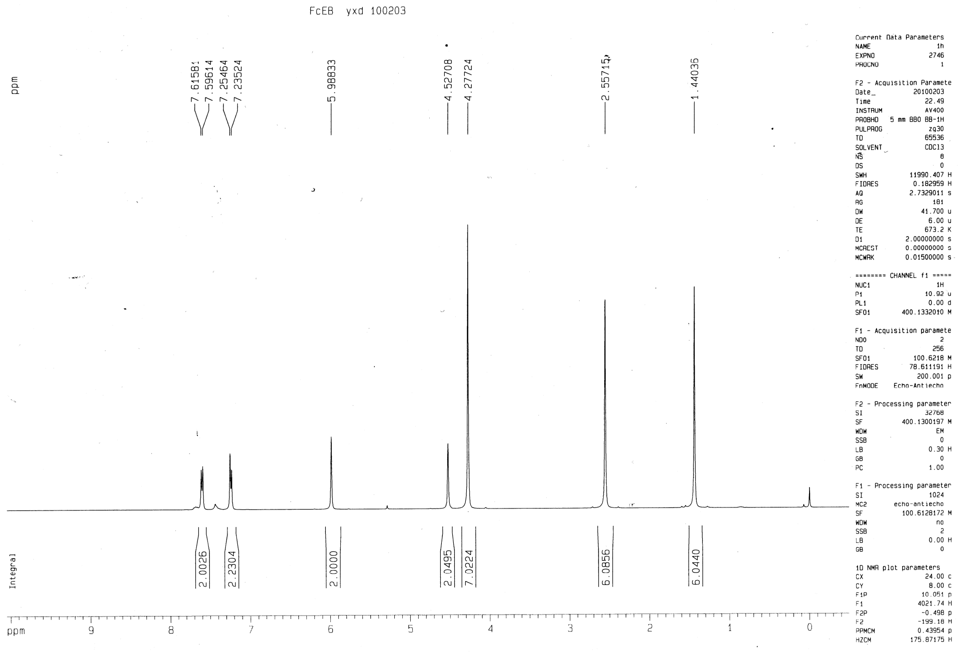
$$\varnothing_F = \varnothing_{st} \frac{S_u}{S_{st}} \frac{A_{st}}{A_u} \frac{n_{Du}^2}{n_{Dst}^2} \qquad (1)$$

Where Φ_F is the emission quantum yield of the sample, Φ_{st} is the emission quantum yield of the standard, $\mathbf{A_{st}}$ and $\mathbf{A_u}$ represent the absorption of the standard and sample at the excitation wavelength, respectively, while $\mathbf{S_{st}}$ and $\mathbf{S_u}$ are the integrated emission band areas of the standard and sample, respectively, and $\mathbf{n_{Dst}}$ and $\mathbf{n_{Du}}$ the solvent refractive index of the standard and sample, **u** and **st** refer to the unknown and standard, respectively.

4-Ferrocenylbenzaldehyde was prepared according to literature procedure.[5] Tetra-n-butylammounium hexfluorophostphate (TBAPF$_6$) used as the supporting electrolyte for the electrochemical measurement was obtained from Alfa-Aesar Co. Ltd., recrystalized and dried in vacuo prior to use. All other reagents were obtained commercially and used as supplied. All the solvents used in electrochemical measurements and photophysical measurements were of HPLC grade quality, purchased and used without further purification unless otherwise noted.

§2. Characterization data

^{1}HNMR of FcEB



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PROCNO                   1

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PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              11990.407 H
FIDRES            0.182959 H
AQ               2.7329011 s
RG                     181
DW                  41.700 u
DE                    6.00 u
TE                   673.2 K
D1              2.00000000 s
MCREST          0.00000000 s
MCWRK           0.01500000 s

======== CHANNEL f1 =====
NUC1                    1H
P1                   10.92 u
PL1                   0.00 d
SFO1           400.1332010 M

F1 - Acquisition paramete
ND0                      2
TD                     256
SFO1              100.6218 M
FIDRES           78.611191 H
SW                 200.001 p
FnMODE       Echo-Antiecho

F2 - Processing parameter
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WDW                     EM
SSB                      0
LB                    0.30 H
GB                       0
PC                    1.00

F1 - Processing parameter
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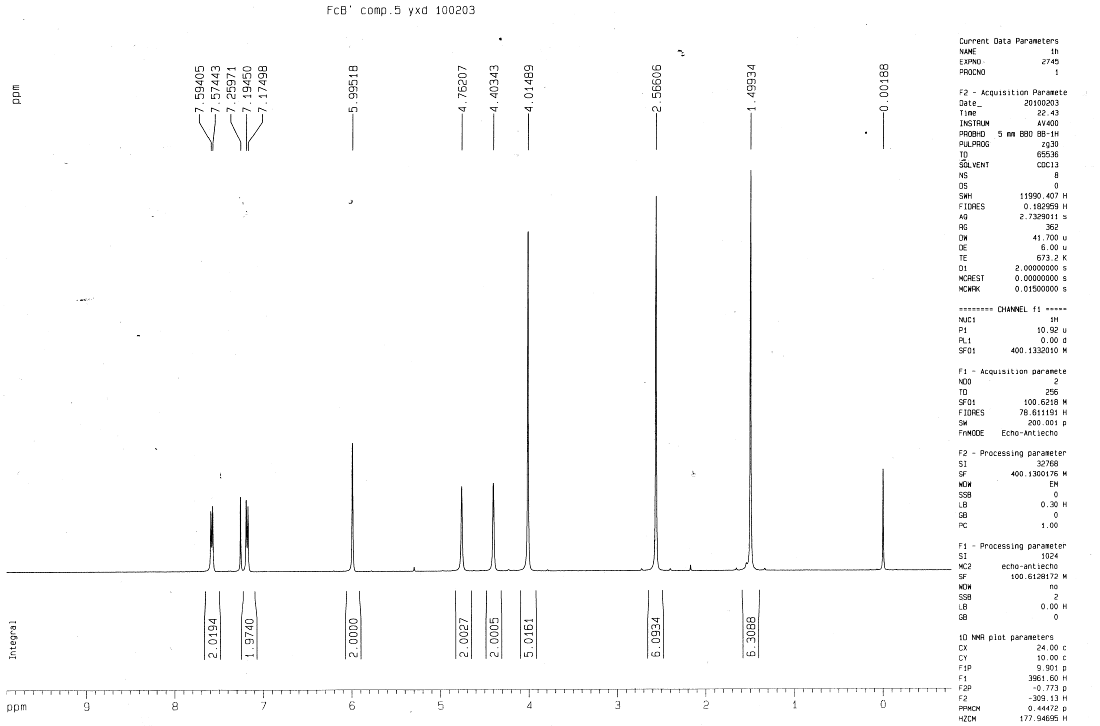
MC2          echo-antiecho
SF             100.6128172 M
WDW                     no
SSB                      2
LB                    0.00 H
GB                       0

1D NMR plot parameters
CX                   24.00 c
CY                    8.00 c
F1P                 10.051 p
F1                 4021.74 H
F2P                 -0.498 p
F2                 -199.18 H
PPMCM              0.43954 p
HZCM             175.87175 H
```

^{13}CNMR of FcEB

^{1}HNMR of FcB



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PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              11990.407 H
FIDRES            0.182959 H
AQ               2.7329011 s
RG                     362
DW                  41.700 u
DE                    6.00 u
TE                   673.2 K
D1              2.00000000 s
MCREST          0.00000000 s
MCWRK           0.01500000 s

======== CHANNEL f1 =====
NUC1                    1H
P1                   10.92 u
PL1                   0.00 d
SFO1           400.1332010 M

F1 - Acquisition paramete
ND0                      2
TD                     256
SFO1              100.6218 M
FIDRES           78.611191 H
SW                 200.001 p
FnMODE      Echo-Antiecho

F2 - Processing parameter
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SF             400.1300176 M
WDW                     EM
SSB                      0
LB                    0.30 H
GB                       0
PC                    1.00

F1 - Processing parameter
SI                    1024
MC2          echo-antiecho
SF             100.6128172 M
WDW                     no
SSB                      2
LB                    0.00 H
GB                       0

1D NMR plot parameters
CX                   24.00 c
CY                   10.00 c
F1P                  9.901 p
F1                 3961.60 H
F2P                 -0.773 p
F2                 -309.13 H
PPMCM              0.44472 p
HZCM             177.94695 H
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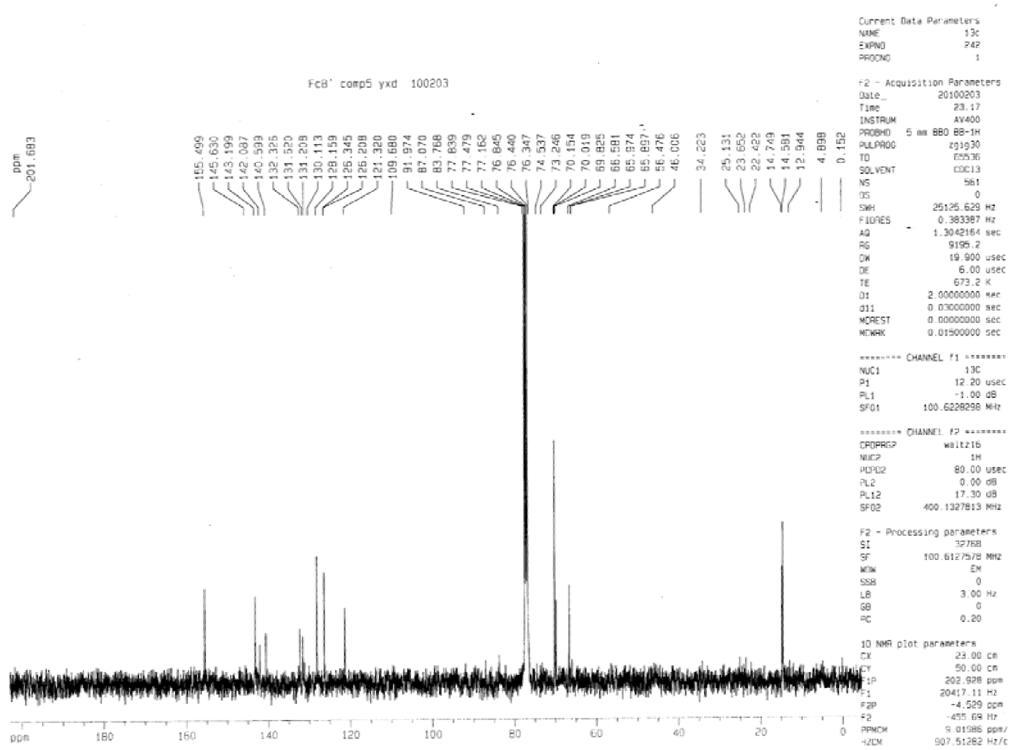
^{13}CNMR of FcB



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TD                    65536
SOLVENT               CDCl3
NS                      561
DS                        0
SWH               25125.629 Hz
FIDRES             0.383387 Hz
AQ                1.3042164 sec
RG                   9195.2
DW                   19.900 usec
DE                     6.00 usec
TE                    673.2 K
D1               2.00000000 sec
d11              0.03000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                    12.20 usec
PL1                   -1.00 dB
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                    0.00 dB
PL12                  17.30 dB
SFO2            400.1327813 MHz

F2 - Processing parameters
SI                    32768
SF              100.6127578 MHz
WDW                      EM
SSB                       0
LB                     3.00 Hz
GB                        0
PC                     0.20

1D NMR plot parameters
CX                    23.00 cm
CY                    50.00 cm
F1P                 202.928 ppm
F1                 20417.11 Hz
F2P                  -4.529 ppm
F2                  -455.69 Hz
PPMCM               9.01986 ppm/
HZCM              907.51282 Hz/c
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§3. Crystal X-ray structure

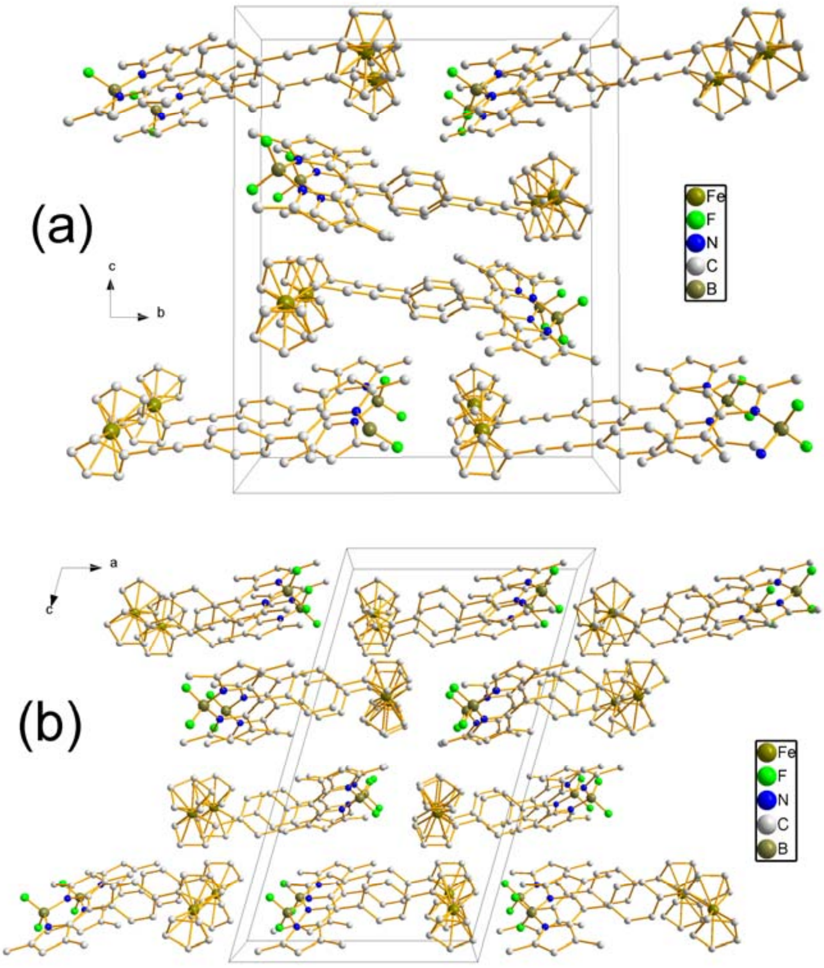

Figure S1. Crystal packing of **FcEB** (a) along the *a* axis and **FcB** (b) along the *b* axis.

§4. Photo-physical property of FcEB, FcB and ethynyl bodipy.

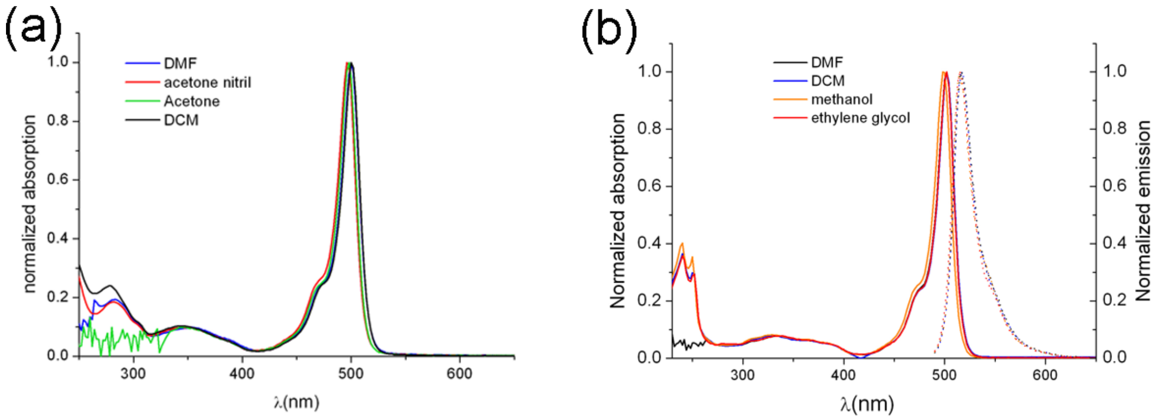

Figure S2. Normalized UV-vis spectra of **FcB(a)** and ethynyl bodipy **(b)**in different solvent.

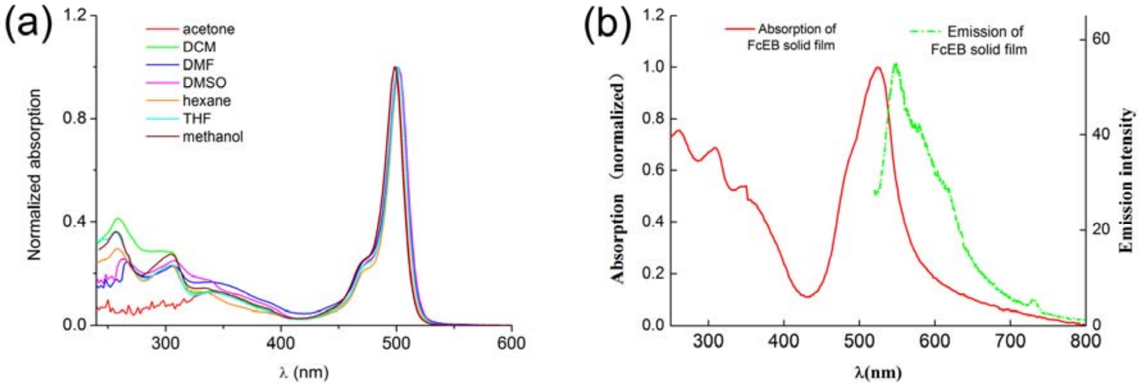

Figure S3 Normalized absorption of **FcEB** in different solvent (a) and solid state (b).

Table S1. Quantum yield of ethynyl BODIPY in different Solvent.

Solvent	**quantum yield**	**viscosity**
DCM	0.84	0.425
THF	0.55	0.55
EG	1	25.66
DMSO	0.89	1.996
DMF	0.75	0.802

Table S2. Literature viscosity of different solvent at 20℃.

solvent	εr	resource
Hexane	1.89	R. W. Dornte and C. P. Smyth, J. Amer. Chem. Soc., 52, 3546(1930)
acetone	20.7	A. A. Mayott et al. ,Table of Dielectric Constants of Pure Liquids, NBS Circular514(1951)
DCM	9.1	Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd ed, Vol. 5, p. 111, Wiley
THF	7.58	C. Marsden, Solvent Guide, 2nd ed. ,p. 514, Cleaver-Hume, 1963.
Methanol	31.2	I. Mellan, Source Book of Industrial Solvents, Vol. 3, p.6~24, Reinhold (1959).
DMF	36.7	A. Wissberger, Organic Solvents (3rd ed.), p. 446, Wiley, 1971
1.4-dioxane	2.2	R. C. little and C. R. Singleterry, J. Phys. Chem. , 86,3453 (1964).
DMSO	48.9	Technical Bulletion Dimethyl Sulfoxide, Dimethyl Sulfoxide as a Reaction Solvents, Crown zellerbach Corp.;U.S.Pat, 3, 045, 051(1962).

Table S3. Literature dielectric constants of different solvent at 20℃

Solvent	Literature Viscosity(20 ℃)	resources
DMF	0.802	A.Wissberger, Organic Solvents (3rd ed), p.446, Wiely,1971
Methanol	0.6	A.Wissberger, Organic Solvents (2nd ed), p.90, Wiely.
THF	0.55	C.Marsden, Solvent Guide, 2nd ed. , p.514, Cleaver-Hume,1963
Hexane	0.307	R.W.Gallant, Hydrocarbon Process. ,46, No. 7, 121(1967)
DMSO	1.996	A.Wissberger, Organic Solvents (3rd ed), p.857, Wiely,1971
Acetone	0.316	C.Marsden, Solvent Manual, p.3, Cleaver-Hume, 1954.
DCM	0.425	Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd ed, Vol.5, p.111, Wiely.
EG	25.66	G. O. Curme and F. Johnoston, Glycols, Van Nostlrand Reinhold, 1952
1,4-dioxane	1.2	C. Marsden, Solvents Guide, 2nd ed. p. 222, Cleaver-Hume, 1963.

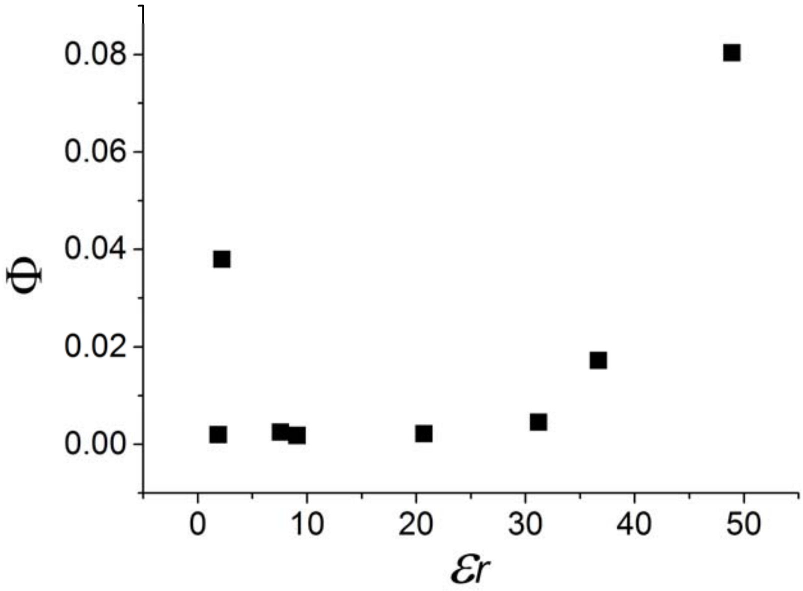

Figure S4. The relationship between the solvent dielectric constant and the quantum yield of **FcEB**

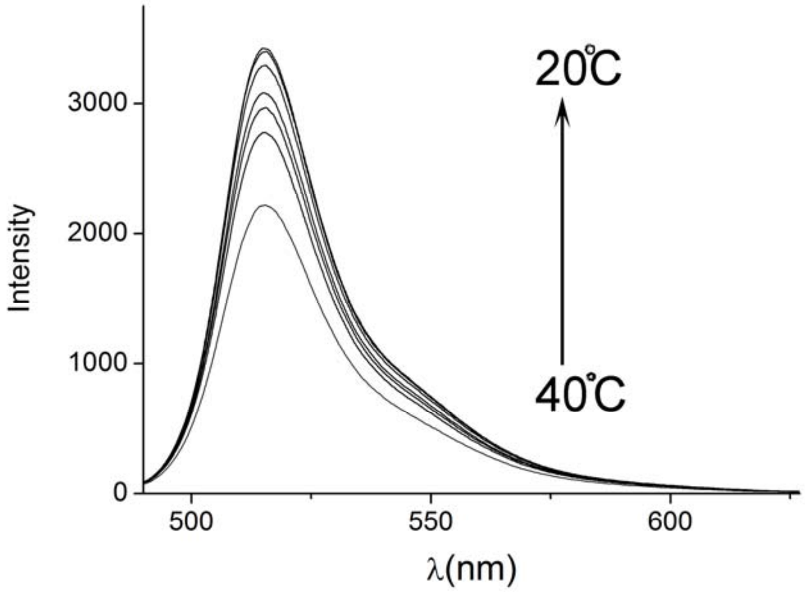

Figure S5. Fluorescence variation as temperature reduced from 40℃ to 20℃ of **FcEB** in mixture of THF/ethylene glycol with the fraction of glycol is 50%.

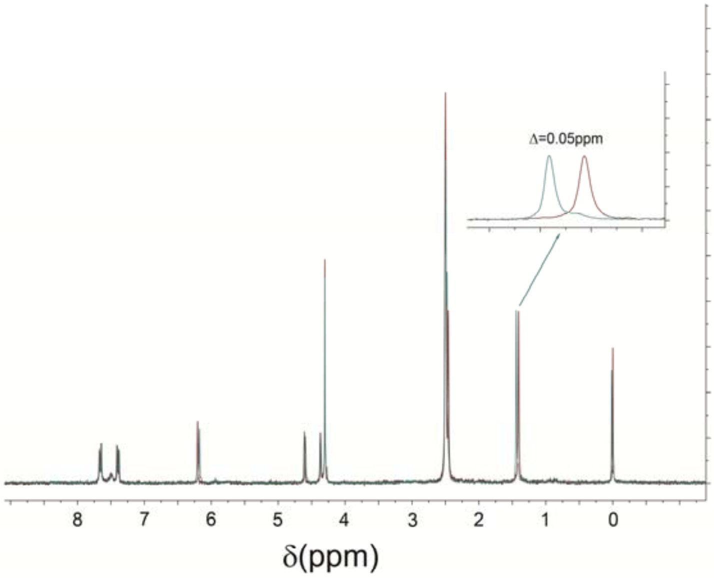

Figure S6. VT-^{1}HNMR of **FcEB** at d^6-DMSO with the temperature from 300K (red line) to 370K (blue line)

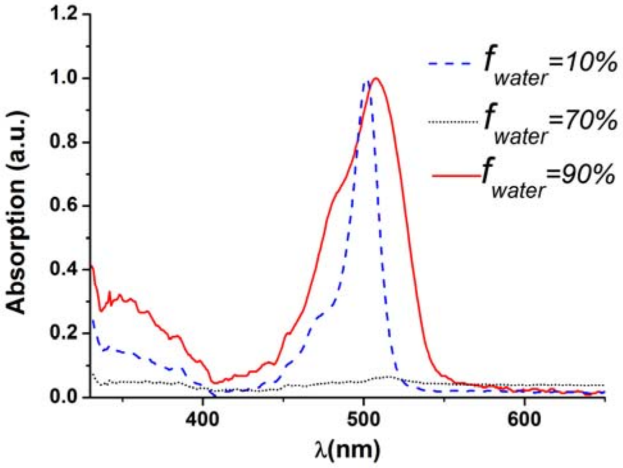

Figure S7. Absorption of **FcEB** in THF/Water mixture with different water fraction.

§5. Spectro-electrochemistry of FcEB

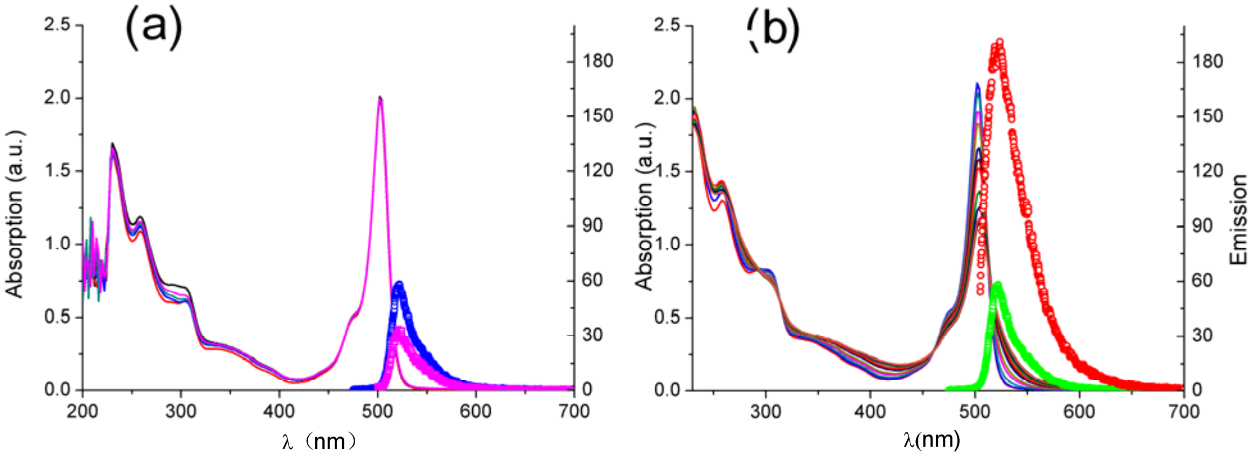

Figure S8. Spectro-electrochemistry experiment for oxidation of **FcEB**. (a) oxidation of **FcEB** under 0.8V for 5min. (b) oxidation of **FcEB** under 1.3V for 5min. The oxidation of ferrocene cannot enhance the emission of **FcEB**, which indicated that the PET process was not the reason of fluorescence quenching of **FcEB** in DCM.

§6. Distribution of **FcEB** in THF/H_2O system

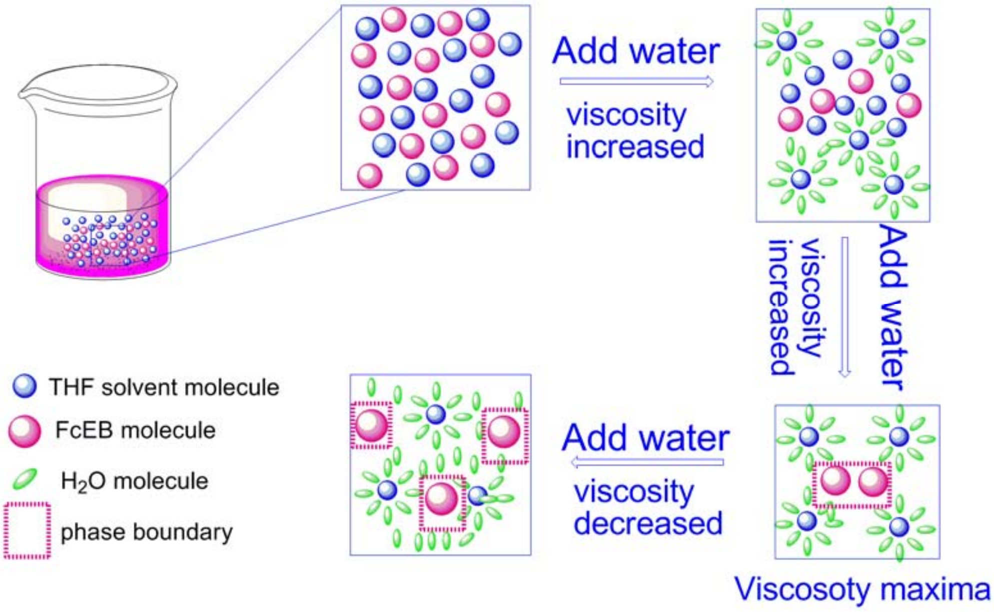

Figure S9. The Change of viscosity of THF/H2O and the distribution mode of FcEB as the water fraction increased

1. K. M. Omer, S. Y. Ku, K. T. Wong and A. J. Bard, *J. Am. Chem. Soc.*, 2009, **131**, 10733-10741.
2. M. Masui, H. Sayo and Y. Tsuda, *J. Chem. Soc. B*, 1968, 973-&.
3. C. A. Parker and W. T. Rees, *Analist*, 1960, **85**, 587-600.
4. J. Chen, A. Burghart, A. Derecskei-Kovacs and K. Burgess, *J. Org. Chem.*, 2000, **65**, 2900-2906.
5. B. J. Coe, C. J. Jones, J. A. Mccleverty, D. Bloor and G. Cross, *J. Organomet. Chem.*, 1994, **464**, 225-232.