SUPPORTING INFORMATION

Two-photon Absorption Enhancement Induced by Aggregation with Accurate Photophysical Data: Spontaneous Accumulation of Dye in Silica Nanoparticles

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Experimental Section

Synthesis and characterization: Elemental analyses were performed with a Perkin-Elmer 240B instrument. Electrospray mass spectrum (ES-MS) was obtained on an API400 mass spectrograph. Mass spectra were determined with a Micromass GCT-MS (EI source). The melting points were measured on a METTLER-TOLEDO DSC822 differential scanning calorimeter at a heating rate of 20 ºC min^{-1} under a nitrogen atmosphere. IR spectra were recorded with a Nicolet FT-IR NEXUS 870 instrument (KBr discs) in the 4000-400 cm^{-1} region. ^{1}H NMR spectra were obtained on Bruker Avance 300 or 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6 solution (with TMS as internal standard). The starting materials and solvents were purchased from Shanghai Chemical Reagent CO., LTD. The solvents were purified by conventional methods before use.

1. **4, 6-Bis-[2-(4-diethylaminophenyl)-vinyl]pyrimidin-2-ol (1)** was synthesized according to reported methods,[1] but the residue was purified by flash chromatography on silica gel using CH2Cl2/methanol (15:1) as elutent. Yield: 80 %。 Mp: >300 ºC. *Anal.* Calc. for $C_{28}H_{34}N_4O$: C, 75.98; H, 7.74; N, 12.66. Found: C, 75.66; H, 7.90; N, 13.10%. IR (KBr, cm^{-1}) selected bands: 3425 (w), 2970 (w), 2928 (w), 1569 (s), 1520 (s), 1350 (m), 1187 (m), 1147 (m), 1075 (w), 970 (w), 812 (w). MS, m/z (%): 442.27 ([M$^+$], 100). **Note that the NMR spectra show prodigious difference compared to the literature.** ^{1}H NMR: (400 MHz, $CDCl_3$), δ (ppm): 1.20 (t, J = 7.01 Hz, 12H), 3.41 (q, J = 7.00 Hz, 8H), 6.66 (d, J = 8.80 Hz, 4H), 6.72 (d, J = 16.00 Hz, 2H), 6.84 (s, 1H), 7.51 (d, J = 8.80 Hz, 4H), 7.76 (d, J = 16.00 Hz, 2H). There are only 9 peak signals in ^{13}C NMR ($CDCl_3$, 100.61 MHz, ppm) δ: 12.66, 44.49, 99.45, 111.34, 122.53, 130.13, 139.70, 149.09, 160.22. And, 10 peak signals in ^{13}C NMR (DMSO-d_6, 100.61 MHz, ppm) δ: 12.94, 44.24, 99.84, 111.84, 117.25, 122.34, 130.13, 139.15, 149.24, 157.87. In two solvents, the same peaks are 8: 12.66, 44.49, 99.45, 111.34, 122.53, 130.13, 139.70 and 149.09. However, there is an extra peak (160.22 ppm) in $CDCl_3$, and two extra peaks (117.25 ppm and 157.87 ppm) in DMSO-d_6. Single crystal X-ray diffraction analysis was used to further verify the structures of the **1**. The crystal structure of compound **1** is shown in Figure

S5, which reveal the structure of **1** is all right.

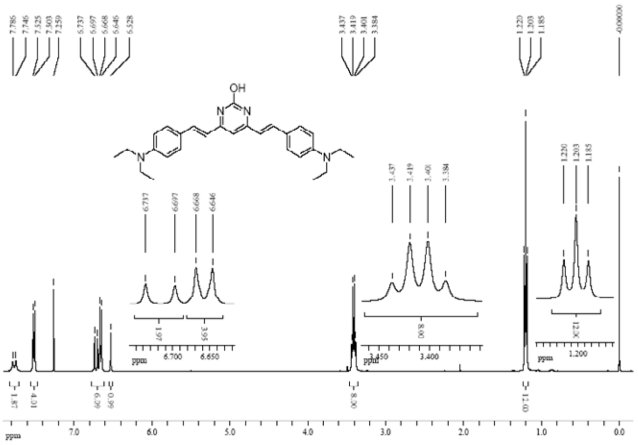


Figure. S1 Proton NMR spectrum of **1** in $CDCl_3$

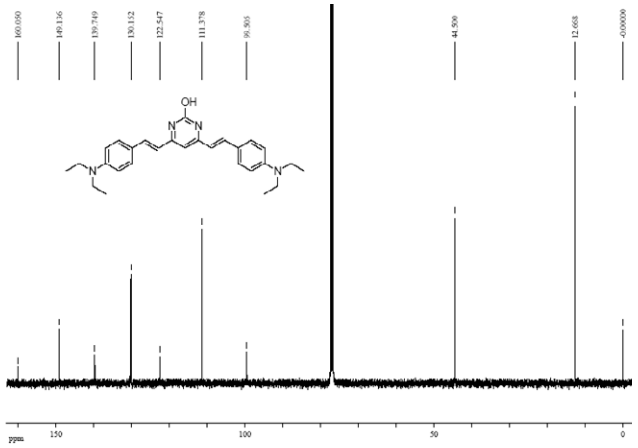


Figure. S2 ^{13}C NMR spectrum of **1** (first time) in $CDCl_3$

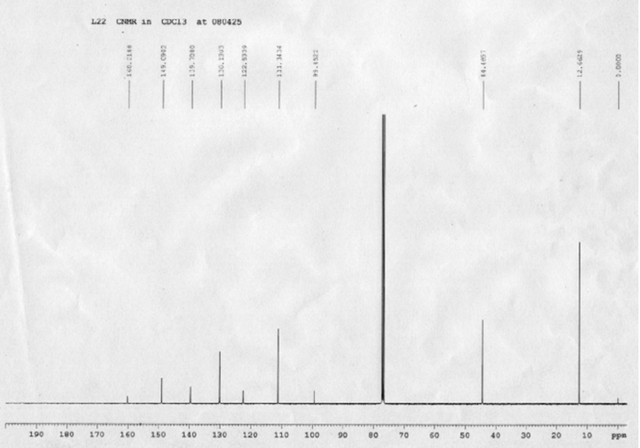


Figure. S3 ^{13}C NMR spectrum of **1** (second time) in $CDCl_3$

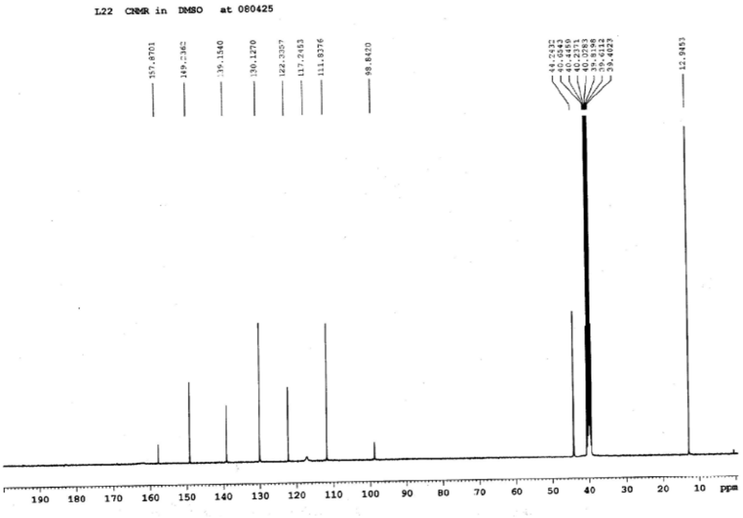


Figure. S4 ^{13}C NMR spectrum of **1** in DMSO-d_6

X-ray crystallography: Data collections were performed using a SMART CCD area detector diffractometer with MoKα radiation with a ω-scan mode [λ=0.71069Å]. The structure was solved with direct methods using the SHELXTL program[2] and refined anisotropically with SHELXTL using full-matrix least-squares procedure. All the nonhydrogen atoms were located form the trial structure and then refined anisotropically with SHELXTL using full matrix least-squares procedure. The hydrogen atom positions were geometrically idealized and allowed to ride on their parent atoms and fixed displacement parameters (Table S1). Table S2 show the selected bond lengths for **1**.

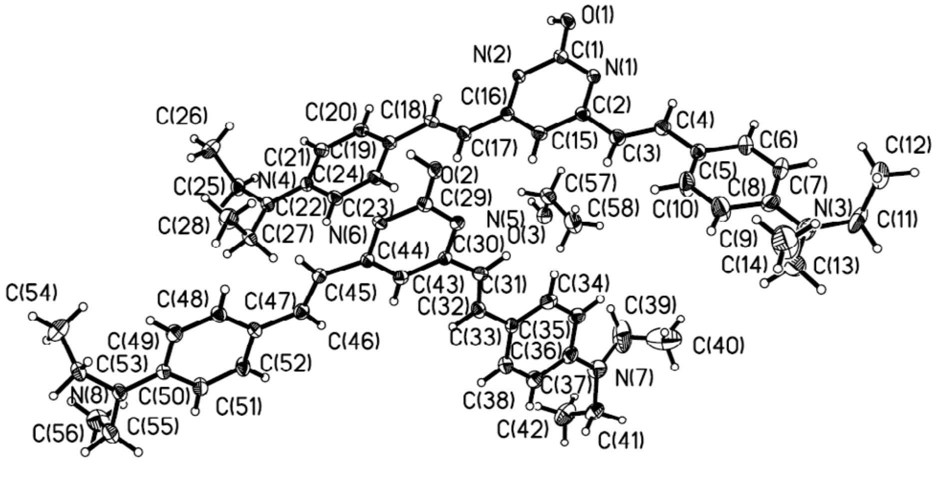


Figure. S5 Crystal structure of **1.**

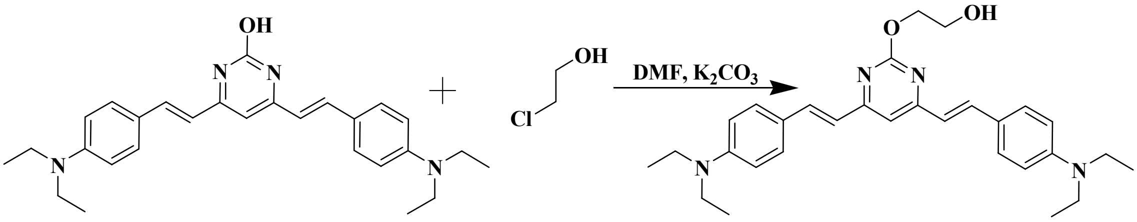
Table S1 Crystallographic data for **1.**

	1
formula	$C_{56}H_{68}N_8O_2 \cdot CH_3CH_2OH$
M_r	931.25
T[k]	293(2)
crystal system	monoclinic
space group	$P2_1/c$
a [Å]	11.2690(14)
b [Å]	12.2153(15)
c [Å]	37.978(4)
α [˚]	90.00
β [˚]	92.248(2)
γ [˚]	90.00
V [$Å^3$]	5223.8(11)
Z	4
F(000)	2008
crystal size [mm^3]	0.15 × 0.15 × 0.12
range [˚]	1,07-25.00
	$-13 \leq h \leq 13$
index range	$-14 \leq k \leq 15$
	$-45 \leq l \leq 38$
data with I>2σ(I)	4380
Goodness-of-fit	1.028
R_{int}	0.1073
R_1 [I>2σ(I)]	0.0779
ωR_2 [I>2σ(I)]	0.2424

Table S2. Selected bond lengths [Å] for **1**

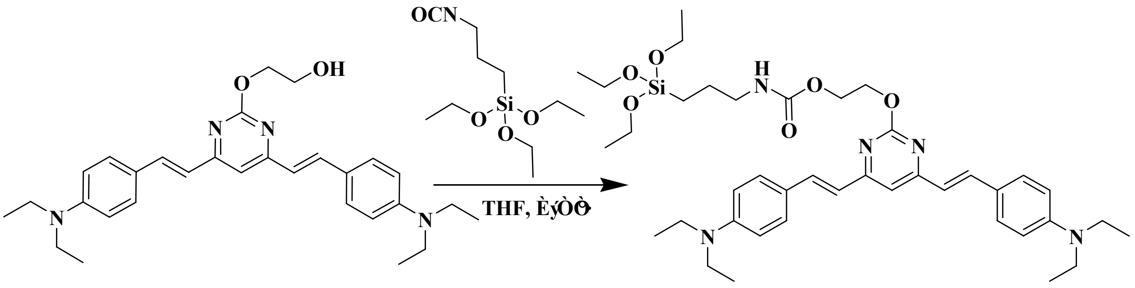
Compound 1			
O1-C1	1.250(4)	O2-C29	1.246(4)
N2-C16	1.372(4)	N6-C29	1.386(5)
N2-C1	1.396(4)	N6-C44	1.377(4)
N1-C2	1.339(5)	N5-C30	1.342(4)
N1-C1	1.357(5)	N5-C29	1.355(5)
C2-C3	1.454(5)	C3-C4	1.340(5)
C4-C5	1.459(5)	C16-C17	1.434(5)
C17-C18	1.342(5)	C18-C19	1.449(5)
C30-C31	1.451(5)	C31-C32	1.316(5)
C32-C33	1.472(5)	C44-C45	1.454(5)
C45-C46	1.339(5)	C46-C47	1.450(5)
C44-C43	1.377(5)	N4-C22	1.370(4)
N4-C25	1.460(5)	N4-C27	1.455(5)
C10-C9	1.371(6)	C2-C15	1.394(5)
N8-C50	1.376(5)	N8-C53	1.459(5)
N8-C55	1.472(5)	C30-C43	1.404(5)
C19-C20	1.396(5)	C19-C24	1.394(5)
C22-C21	1.391(5)	C22-C23	1.408(5)

C48-C49	1.362(5)	C48-C47	1.387(5)
C11-N3	1.456(6)	C11-C12	1.506(7)
C16-C15	1.372(5)	C21-C20	1.376(5)
C23-C24	1.373(5)	C49-C50	1.410(7)
C34-C35	1.384(6)	C34-C33	1.392(5)
C47-C52	1.393(5)	C50-C51	1.398(5)
C5-C6	1.381(5)	C5-C10	1.374(6)
C52-C51	1.366(5)	C33-C38	1.384(5)
N7-C36	1.378(5)	N7-C41	1.456(5)
N7-C39	1.532(8)	C25-C26	1.508(6)
C13-N3	1.493(7)	C13-C14	1.508(8)
C38-C37	1.380(5)	C8-C7	1.396(6)
C6-C7	1.378(6)	C53-C54	1.509(6)
C8-C9	1.408(6)	N3-C8	1.376(5)
C36-C35	1.386(6)	C36-C37	1.399(5)
C27-C28	1.512(6)	C55-C56	1.502(6)
C40-C39	1.410(9)	C41-C42	1.495(6)



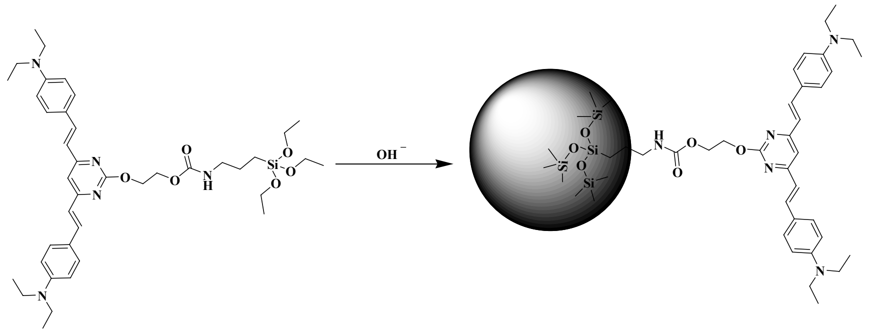
Scheme S1 Strategies for preparation of dye.

2．4, 6-Bis-[2-(4-diethylaminophenyl)-vinyl]pyrimidin-2-(2’-hydroxy)ethyloxyl (dye): As shown in Scheme S1, **1** (0.44 g，1 mmol), chlorohydrin (0.16 g，2 mmol) and K_2CO_3 (0.27 g，2 mmol) were mixed in 30 mL dry DMF. The reaction mixture was stirring at 80 ºC over 48 h. After the reaction was completed, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel using CH_2Cl_2/methanol (25:1) as elutent and gave red solid 350 mg. Yield: 72%. *Anal.* Calc. for $C_{30}H_{38}N_4O_2$: C, 74.04; H, 7.87; N, 11.51. Found: C, 74.36; H, 7.90; N, 11.10 %. IR (KBr, cm^{-1}) selected bands: 3396 (m), 2972 (m), 1604 (m), 1567 (s), 1518 (m), 1405 (m), 1152 (m), 1079 (m), 1055 (m), 814 (w). ^1H NMR: (400 MHz, $CDCl_3$), δ (ppm): 1.20 (t, J = 7.01 Hz, 12H), 3.41 (q, J = 6.80 Hz, 8H), 4.03 (s, 2H), 4.64 (s, 2H), 6.69 (d, J = 6.40 Hz, 4H), 6.75 (s, 1H), 6.82 (d, J = 18.40 Hz, 2H), 7.47 (d, J = 8.40 Hz, 4H), 7.79 (d, J = 15.60 Hz, 2H). MS, m/z (%): 486.16 ([M$^+$], 100). ^{13}C NMR (CDCl$_3$, 100.61 MHz, ppm) δ: 12.62, 44.57, 62.50, 69.37, 110.18, 111.54, 120.15, 123.05, 129.53, 137.57, 148.57, 165.24, 165.45.



Scheme S2 Strategies for preparation of precursor.

3. Precursor: As shown in Scheme S2, the functional dye (0.49 g，1 mmol) was stirred in 10 mL dry triethylamine at 80 ºC for 2 h。3-isocyanatopropyltriethoxysilane (ICTES, 5 mL) was added in the solvent and was stirred for 24h. After the reaction was completed, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel using CH_2Cl_2/methanol (45:1) as elutent and gave red solid 150 mg. Yield: 31%. *Anal.* Calc. for $C_{40}H_{59}N_5O_6Si$: C, 65.45; H, 8.10; N, 9.54. Found: C, 65.23; H, 7.91; N, 10.02 %. IR (KBr, cm^{-1}) selected bands: 3409 (m), 2963 (s), 2854 (m), 1732 (m), 1602 (s), 1564 (s), 1519 (s), 1403 (m), 1356 (m), 1262 (s), 1080 (s), 967 (m), 802 (s). ^{1}H NMR: (400 MHz, CDCl$_3$), δ (ppm): 0.51 (t, *J* = 8.4, 2H), 1.20 (t, *J* = 7.01 Hz, 12H), 1.37 (t, *J* = 7.0, 9H), 1.44 (m, 2H), 2.92 (t, *J* = 6.8, 2H), 3.41 (q, *J* = 6.80 Hz, 8H), 3.80 (q, *J* = 6.8, 6H), 4.50 (s, 2H), 4.68 (s, 2H), 6.64 (d, *J* = 6.40 Hz, 4H), 6.75 (s, 1H), 6.82 (d, *J* = 16.40 Hz, 2H), 7.47 (d, *J* = 8.40 Hz, 4H), 7.82 (d, *J* = 15.60 Hz, 2H). MS, m/z (%): 733.43 ([M$^+$]).



Scheme S3 Strategies for preparation of DCNs.

4. DCNs: W/O microemulsion was prepared by mixing 1 mL of water, 5.3 mg of NaOH, and 410 mg of 1-butanol in THF (10 mL). The mixture was stirred at room temperature for 30 min. Precursor (96 mg) dissolving in 5 mL of THF was added dropwise under stirring, which was left stirring for 7 days. After hydrolysis completed, DCNs was separated from the solvent by centrifugation (washed with EtOH until there is colorless of the ethanol) and purified by Soxhlet extraction with ethanol for 24 h. After drying under a vacuum for more than 48 h for complete removal of 1-butanol and any other solvent, the average weight of a batch of DCNs was around 39 mg. IR (KBr, cm^{-1}) selected bands: 3421 (w), 2970 (s), 2927 (w), 1702 (w), 1602 (m), 1564 (s), 1520 (s), 1404 (w), 1356 (w), 1267 (m), 1147 (m), 972 (w), 807 (w).

Detail of optical spectra

Optical measurements. Electronic spectra were recorded on a UV-3600 spectrophotometer. The one-photon fluorescence spectra measurement is performed with use of an F-2500 Spectro-fluorophotome. Spectra are recorded between 400 and 800 nm using a photomultiplier tube as detector. Time-resolved decay curves were measured by fluotime200 (Pico Quant). The TPEF spectra were measured using a mode-locked Ti: sapphire laser (Coherent Mira900F) as pump source with pulse duration of 120 fs, a repetition rate of 80 MHz, and a single-scan streak camera (Hamamastu Model C5680-01) together with a monochromator as the recorder. The set-up for TPEF measurements is shown in Figure S6.

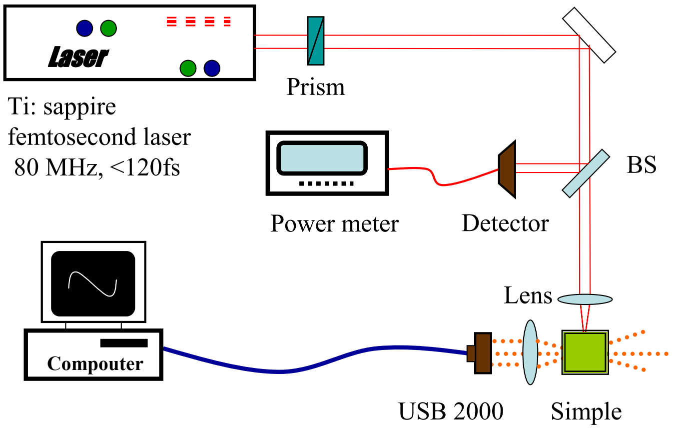


Figure S6 The experimental setup for TPEF measurement at different excitation wavelengths

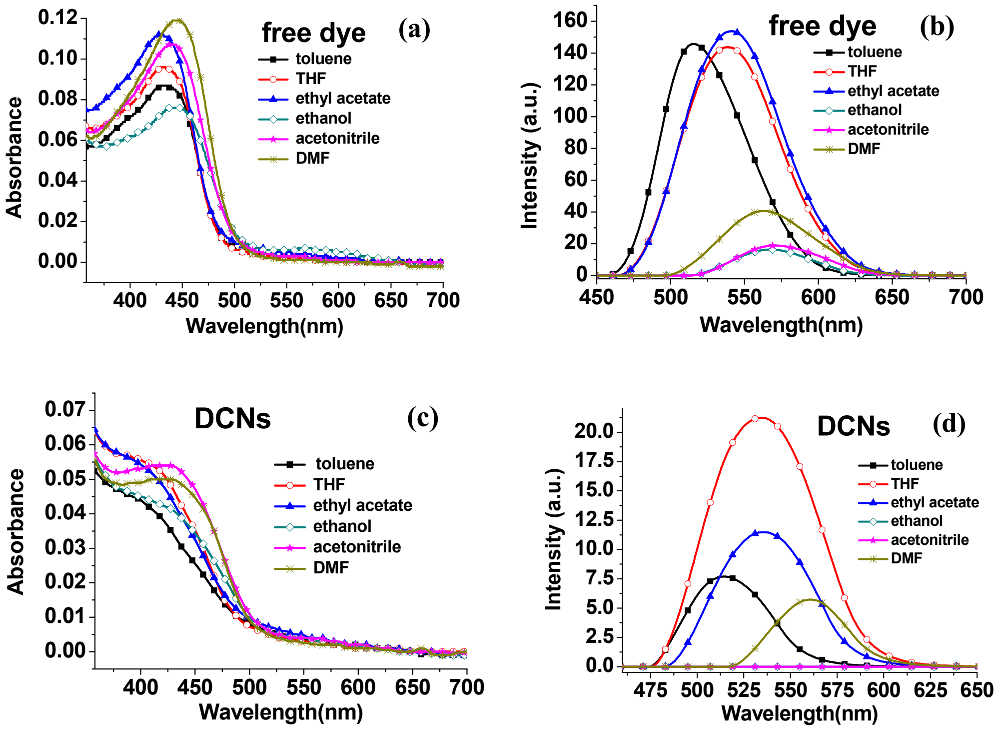


Figure S7 Single-photon absorption and Single-photon excited fluorescence spectrum of the free dye (a and b) and DCNs (c and d) in several solvents with differing polarity.

Table S3 The linear photophysical properties of the free dye and DCNs in different polar solvents.

compd	Solvents	$\lambda_{max}^{(1a)}$ [a]	$\lambda_{max}^{(1f)}$ [b]	Φ[c]	$\Delta\nu$ [d]	τ[ns]
free dye	toluene	433	514	0.52	3639	
	THF	434	538	0.47	4454	
	ethyl acetate	428	540	0.43	4845	
	ethanol	443	569	0.20	4998	
	acetonitrile	439	579	0.25	5507	
	DMF	445	561	0.36	4647	2.60/1.57
DCNs	toluene	399	513	0.12	5569	
	THF	406	533	0.26	5868	
	ethyl acetate	395	533	0.15	6555	
	ethanol	428	-	0	-	
	acetonitrile	423	-	0	-	
	DMF	431	560	0.10	5345	2.52/0.86

[a] Peak position of the longest absorption band. [b] Peak position of SPEF, exited at the absorption maximum. [c] Quantun yields determined by using coumarin as standard. [d] Stokes' shift in cm^{-1}. There are negligible in the emission for DCNs in ethanol and acetonitrile.

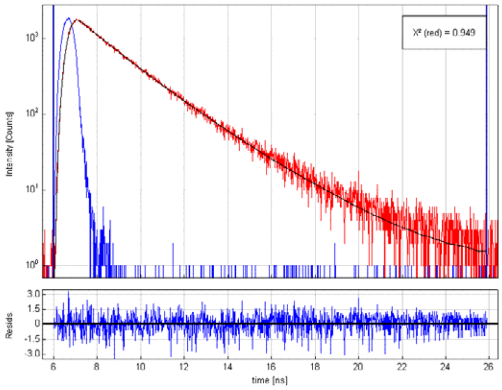


Figure S8 Decay curves of the free dye in DMF and the fitting result of the corresponding lifetimes

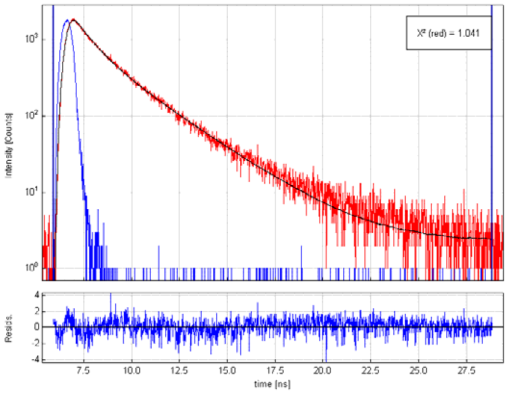


Figure S9 Decay curves of DCNs in DMF and the fitting result of the corresponding lifetimes

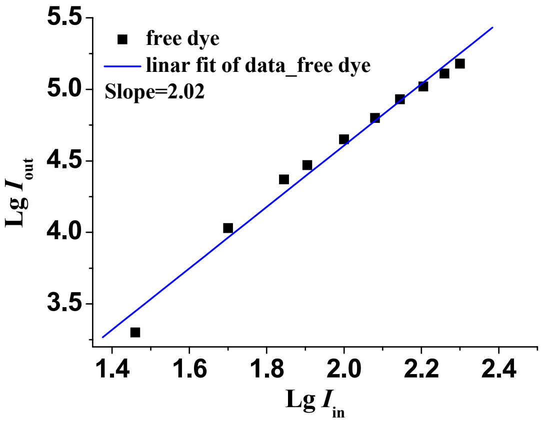


Figure S10 Output fluorescence (I_{out}) *vs*. the square of input laser power (I_{in}) for the free dye in DMF.

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1. Liu, Z. J.; Chen, T.; Liu, B.; Huang, Z. L.; Huang, T.; Li, S. Y.; Xua Y. X.; Qin, J. G. *J. Mater. Chem.* **2007**, *17*, 4685.
2. MOLEKEL, references in http://www.cscs.ch/molekel/