Electronic Supplementary Information for

Water-Tunable Solvatochromic and Nanoaggregate Fluorescence: Dual Colour Visualisation and Quantification of Trace Water in Tetrahydrofuran

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Fig. S14 Water content dependent fluorescence spectra of *trans*-ABPX103^{0} in THF solution.

3. References

1. General remarks

Fluorescence quantum yields measurement. The fluorescence quantum yields in solution were determined by a HORIBA FluoroMax-4 spectrofluorometer by using a calibrated integrating sphere system.

Dynamic laser light scattering (DLS) measurement. The particle-size distributions were measured with Zetasizer Nano Series at 25 °C (Malvern) using a 1cm quartz cuvette (PCS1115).

Video image. The video image of naked eye visualisation of water at content above 0.5 wt% in THF was taken under the irradiation of 365 nm light with a digital hi-vision video camera of Panasonic HC-V520M. In advance, 2.5 ml of dehydrated THF was contained in left cuvette, and 2.5 ml of 0.5 wt% water/THF was contained in the right cuvette. Then 5 mM of *trans*-ABPX103^0 dissolved in dehydrated THF was poured into each cuvette (final concentration of *trans*-ABPX103^0 was 1 mM).

2. Figures and tables

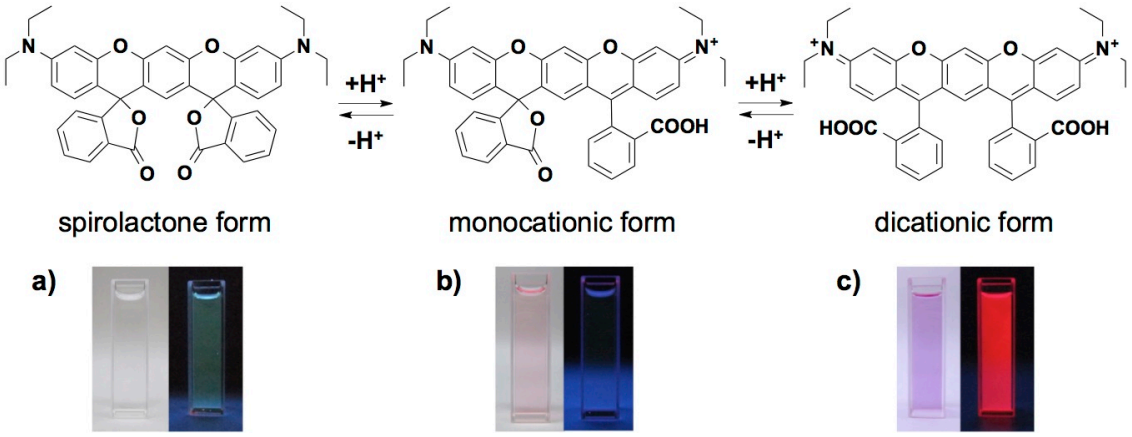

Fig. S1 Protolytic equilibria of ABPX01.[1,2] The spirolactone form of ABPX01 is changed to the monocationic form and the dicationic form as the proton is added. Photographs represent the respective chemical species under room light (left) and 365 nm UV irradiation (right) in (a) THF solution (spirolactone form), (b) 1 % TFA/THF mixture (monocationic form), and (c) 1 % TFA/ chloroform mixture (dicationic form).

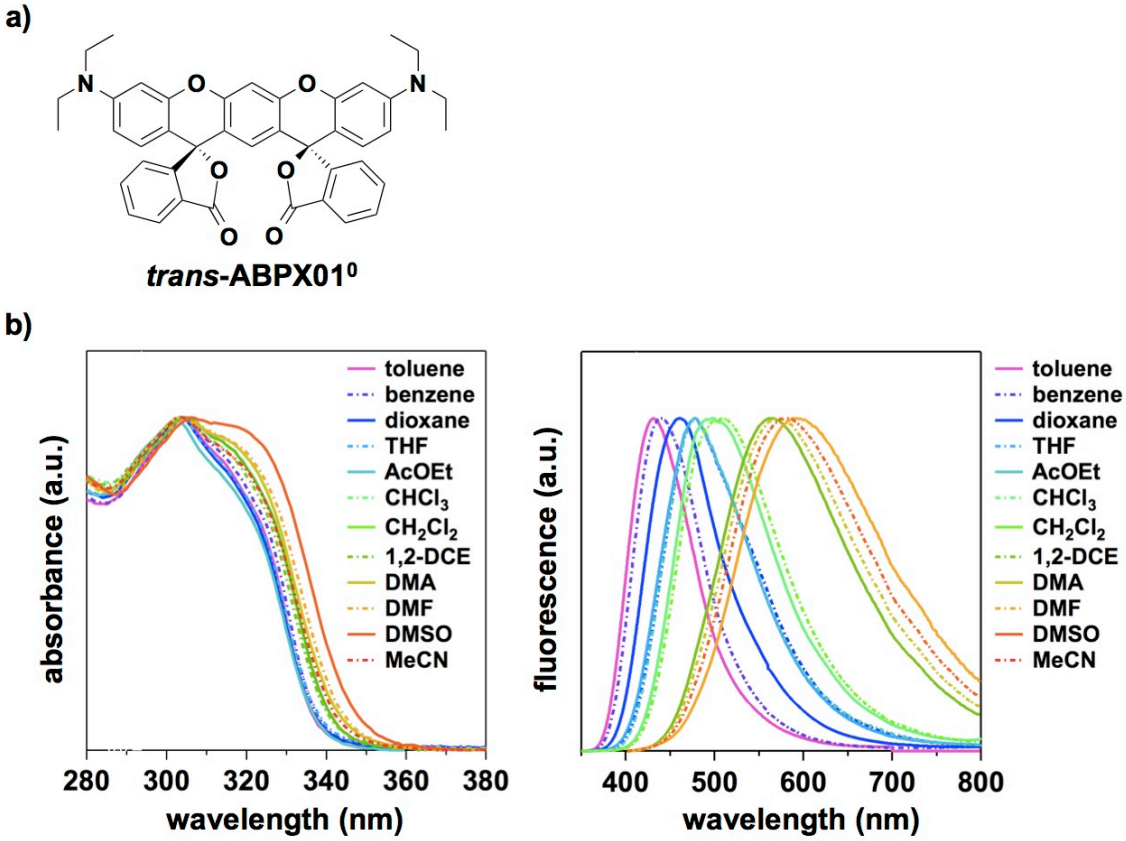

Fig. S2 (a) Chemical structure of *trans*-ABPX01^0. (b) Absorption (left) and fluorescence (right) spectra of *trans*-ABPX01^0 (200 μM) in toluene, benzene, 1,4-dioxane (dioxane), tetrahydrofuran (THF), ethyl acetate (AcOEt), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), 1,2-dichloroethane (1,2-DCE), *N,N*-dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and acetonitrile (MeCN). λ_{ex} = 305 nm.

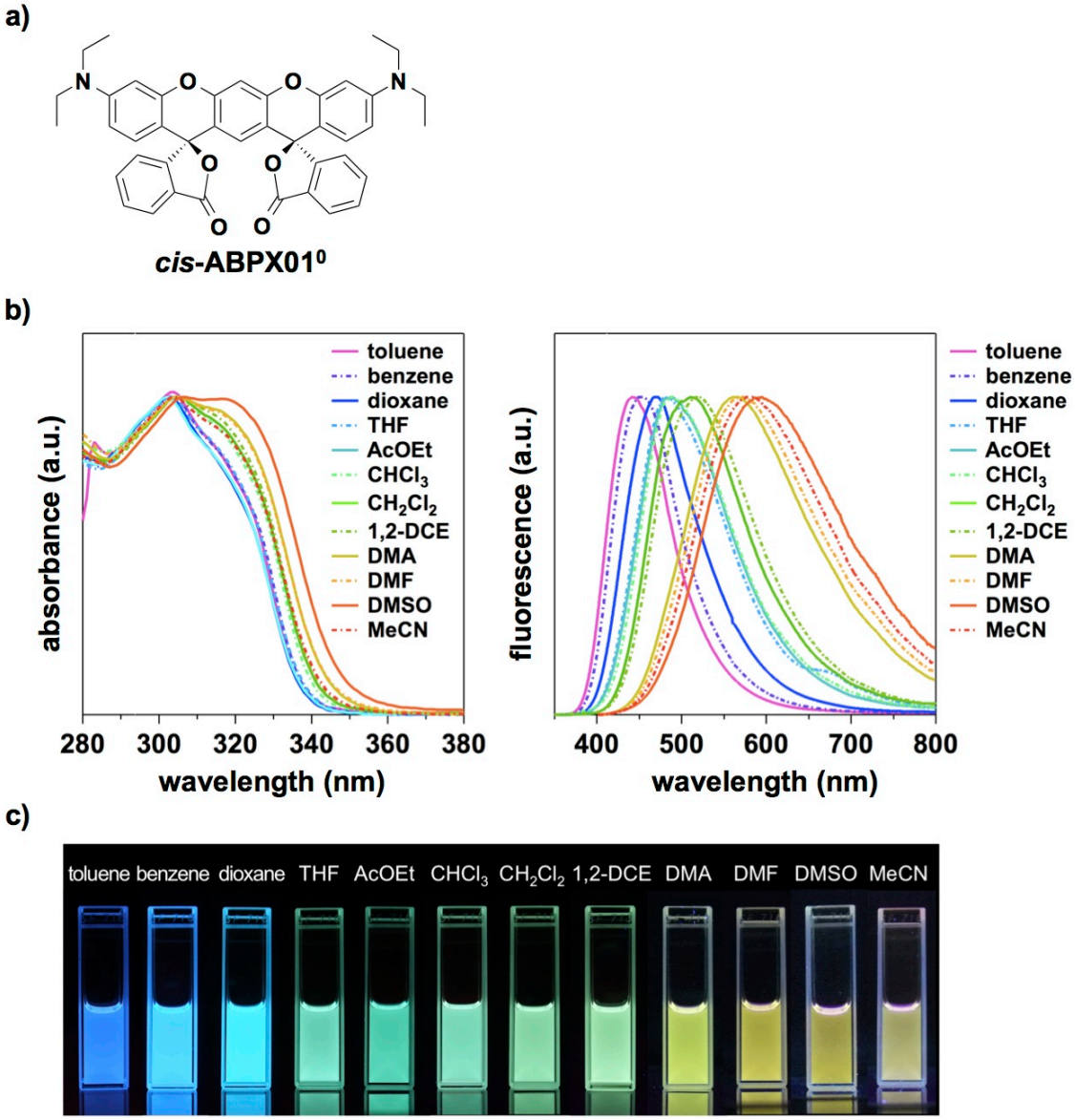

Fig. S3 (a) Chemical structure of *cis*-ABPX01^0. (b) Absorption (left) and fluorescence (right) spectra of *cis*-ABPX01^0 (200 μM) in organic solvents of different polarities. λ_{ex} = 305 nm. (c) Photograph of the solvatofluorochromic shift of *cis*-ABPX01^0 in organic solvents.

Table S1. Optical properties of *cis*-ABPX01^{0} [*1].

solvent	$E_T(30)$	λ_{abs}	λ_{fl} [*2]	ε	Stokes shift	
	[kcal mol^{-1}]	[nm]	[nm]	[M^{-1} cm^{-1}]	[nm]	[cm^{-1}]
toluene	33.9	304	441	25400	137	10219
benzene	34.3	304	451	26400	147	10722
dioxane	36.0	303	471	27300	168	11772
THF	37.4	303	480	28300	177	12170
AcOEt	38.1	302	488	31900	186	12621
$CHCl_3$	39.1	305	489	28800	184	12337
CH_2Cl_2	40.7	305	510	27900	205	13179
1,2-DCE	41.3	305	518	25800	213	13482
DMA	42.9	305	559	27500	254	14898
DMF	43.2	304	567	26900	263	15258
DMSO	45.1	307	578	25800	271	15272
MeCN	45.6	304	576	27600	272	15534

[*1] The dye concentration was 200 μM. [*2] λ_{ex} = 305 nm.

Table S2. Fluorescence quantum yields of *trans*- and *cis*-ABPX01^{0} [*1].

	***trans*-ABPX01^{0}**	***cis*-ABPX01^{0}**
toluene	0.6	1.3
benzene	2.9	6.1
1,4-dioxane	0.9	1.2
THF	1.0	1.4
AcOEt	2.9	0.6
$CHCl_3$	2.3	1.6
CH_2Cl_2	3.9	2.3
1,2-DCE	1.5	1.2

[*1] The dye concentration was 20 μM. λ_{ex} = 320 nm.

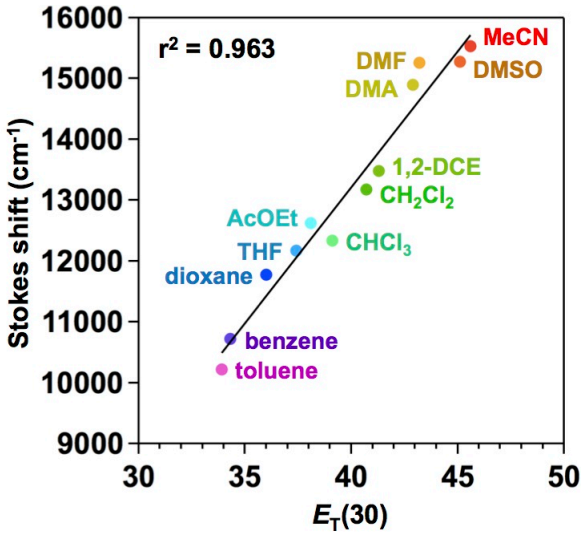

Fig. S4 Correlation of Stokes shift of *cis*-ABPX01^0 to the solvent polarity index $E_T(30)$.

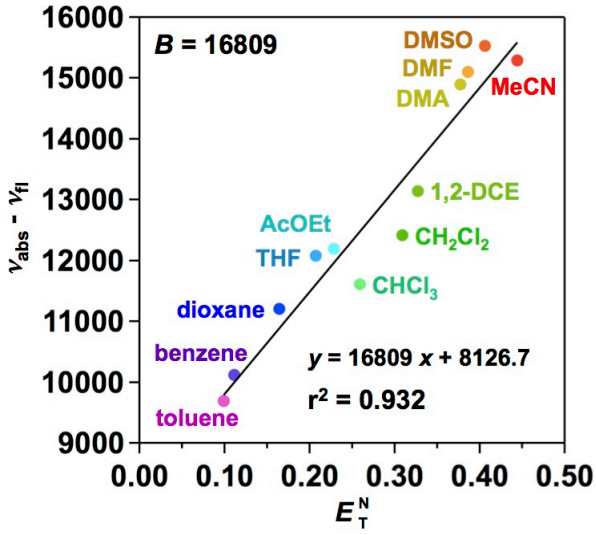

Fig. S5 Plot of $\nu_{abs} - \nu_{fl}$ versus E_T^N for *trans*-ABPX01^0 in different organic solvents.

Table S3. Optical properties of *trans*-ABPX103^{0} [*1].

solvent	$E_T(30)$	λ_{abs}	λ_{fl} [*2]	ε	Stokes shift	
	[kcal mol^{-1}]	[nm]	[nm]	[M^{-1} cm^{-1}]	[nm]	[cm^{-1}]
toluene	33.9	307	473	22900	166	11432
benzene	34.3	308	478	24100	170	11547
dioxane	36.0	305	490	23800	185	12379
THF	37.4	305	525	25100	220	13739
AcOEt	38.1	304	532	21000	228	14098
$CHCl_3$	39.1	307	534	24500	227	13847
CH_2Cl_2	40.7	309	559	24700	250	14473
1,2-DCE	41.3	308	572	21400	264	14985
DMA	42.9	307	616	22000	309	16340
DMF	43.2	307	583	21500	276	15421
DMSO	45.1	324	596	21400	272	14086

[*1] The dye concentration was 200 μM. [*2] λ_{ex} = 305 nm.

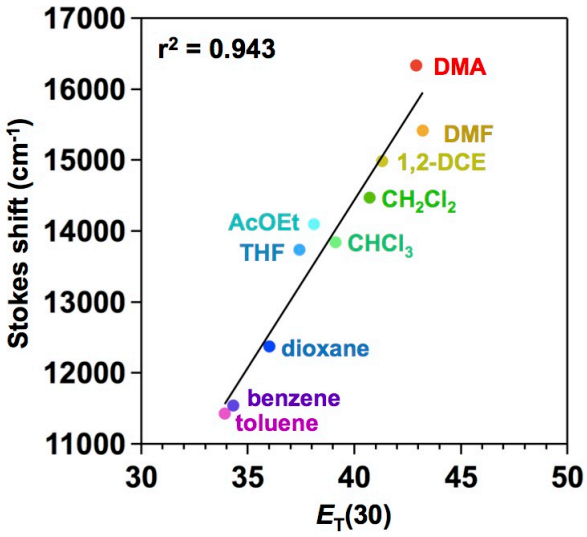

Fig. S6 Correlation of Stokes shift of *trans*-ABPX103^{0} to the solvent polarity index $E_T(30)$.

Table S4. Crystal data and structure refinement parameters for *trans*-ABPX103[0].

included solvent	$CHCl_3$	**D_{calcd}, g/cm^3**	1.421
crystal system	monoclinic	**T, K**	100.15
space group [No.]	$P2_1$ [#4]	**radiation[a]**	Mo Kα
crystal color, habit	red, prism	**μ, mm^{-1}**	0.3695
crystal size, mm	0.15 × 0.08 × 0.07	**$2\theta_{max}$, °**	54.8
a, Å	9.374(7)	**F(000)**	1844.0
b, Å	35.90(3)	**reflns collected**	37634
c, Å	12.405(9)	**unique reflns**	18238
α, °	90	**No. of parameters**	1081
β, °	93.387(6)	**$R1$ (I > 2.00σ(I))**	0.0761
γ, °	90	**R (all reflection)**	0.0988
volume, Å^3	4167(6)	**GOF**	1.090
Z	2	**CCDC No.**	1487915

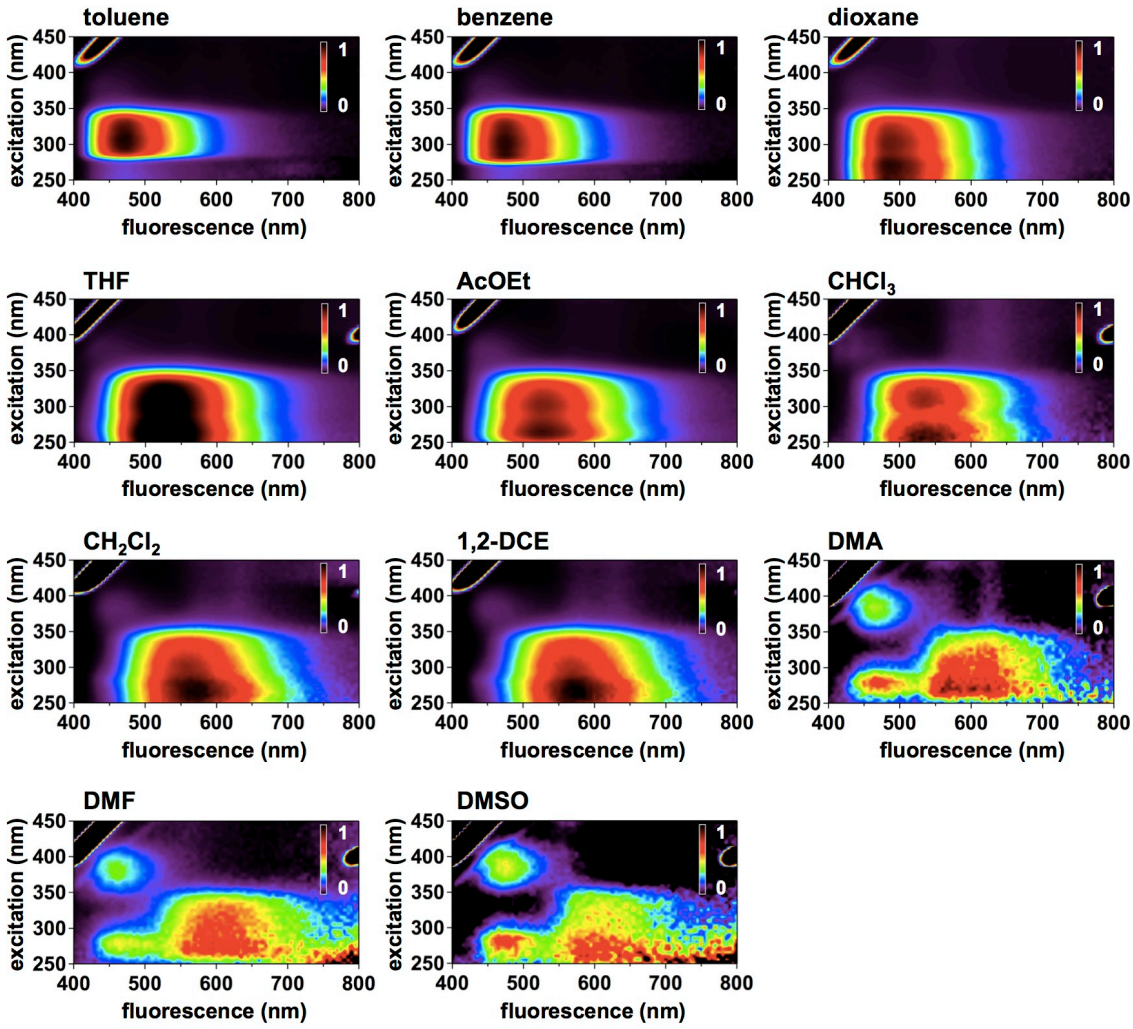

Fig. S7 Fluorescence-Excitation Matrix (FEM) spectra of *trans*-ABPX103^0 in various solvents.

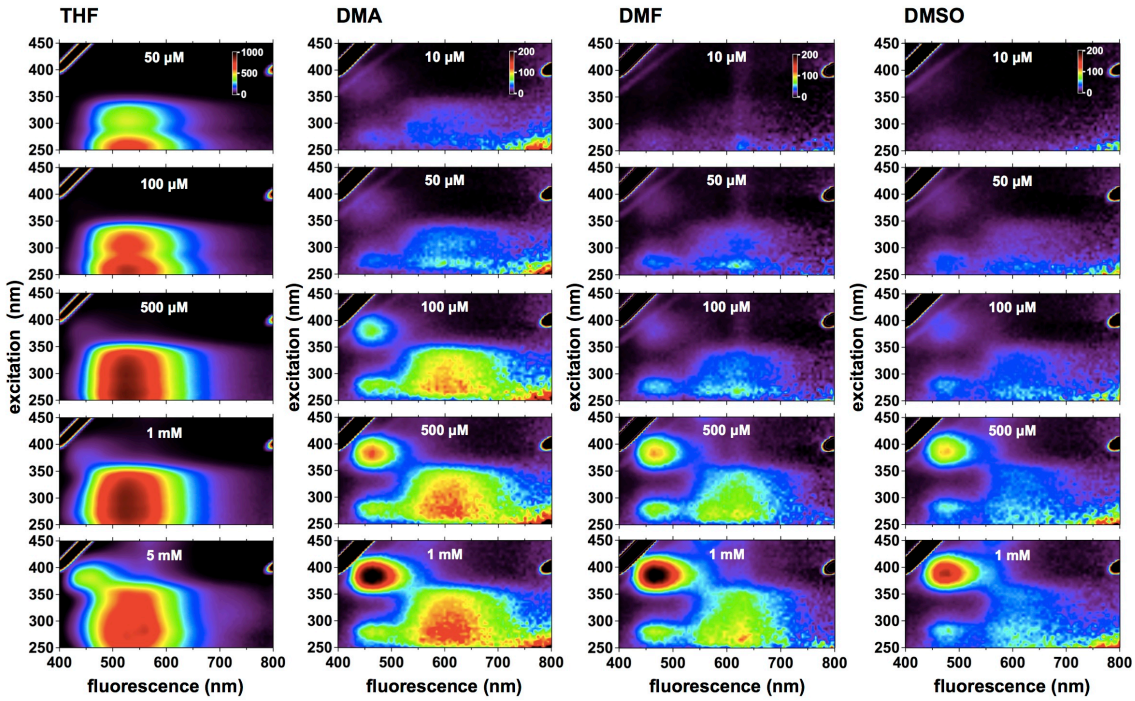

Fig. S8 Concentration dependent FEM spectra of *trans*-ABPX103^0 in THF, DMA, DMF, and DMSO.

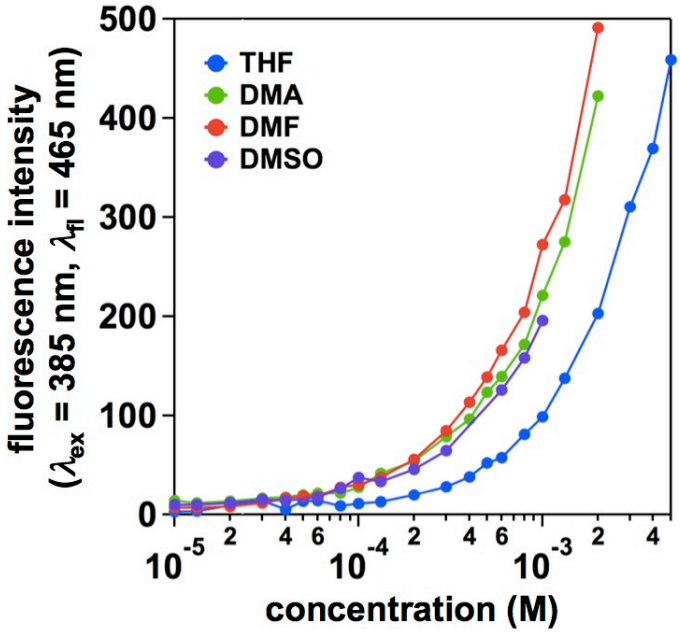

Fig. S9 Concentration dependent intensities of aggregate fluorescence peak of *trans*-ABPX103^{0} in THF, DMA, DMF, and DMSO.

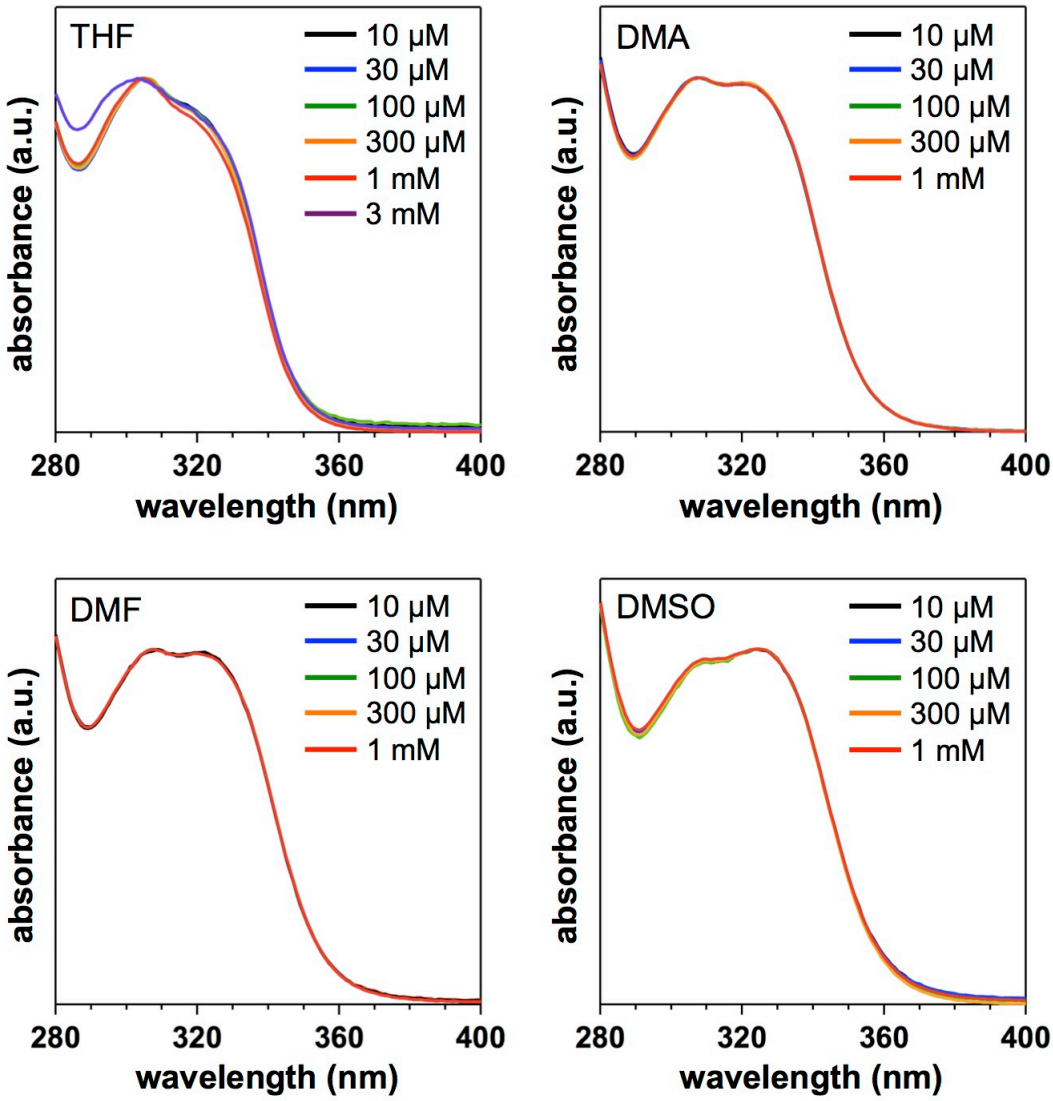

Fig. S10 Concentration dependent absorption spectra of *trans*-ABPX103^{0} in THF, DMA, DMF, and DMSO.

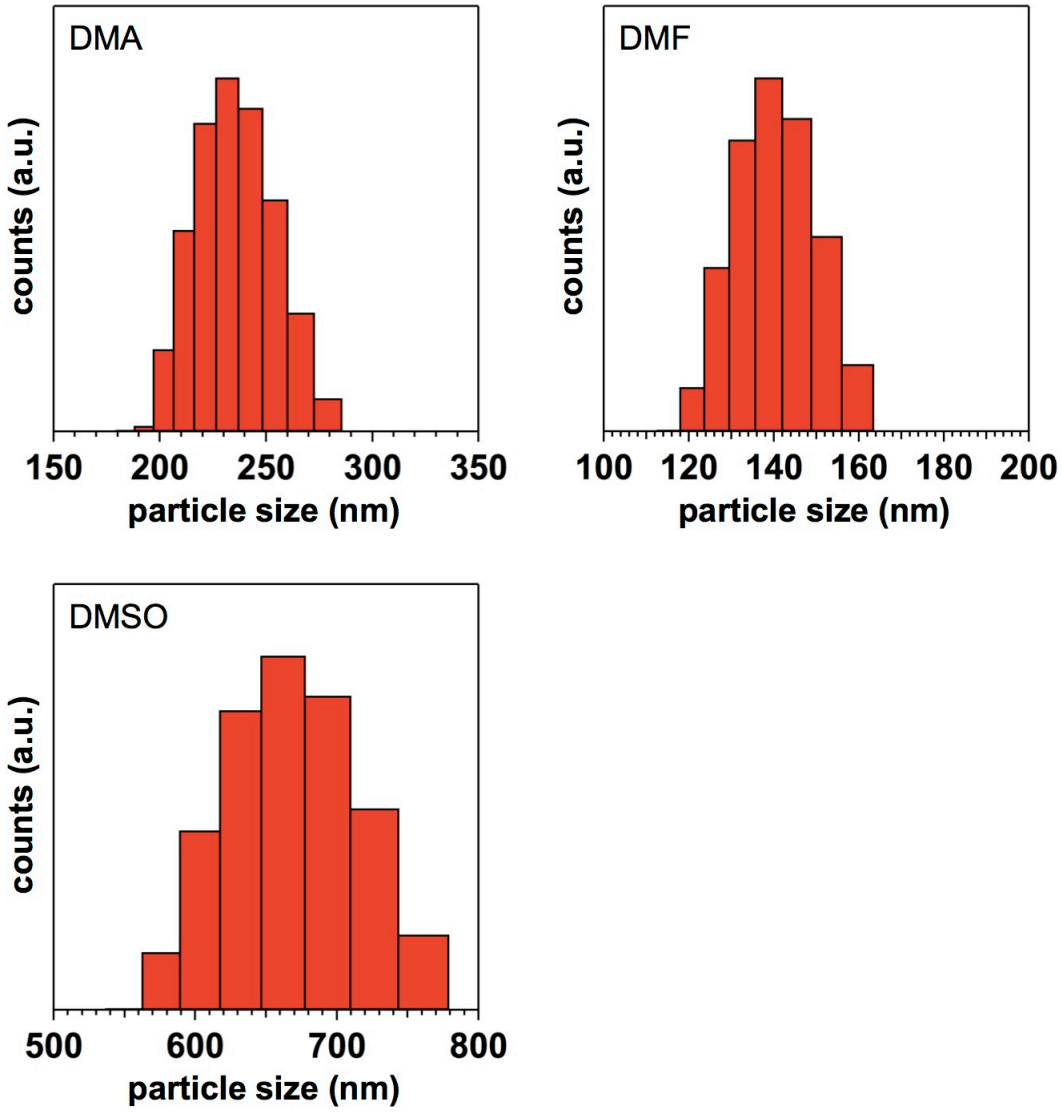

Fig. S11 Dynamic laser light scattering of 1 mM *trans*-ABPX103^0 in DMA, DMF and DMSO.

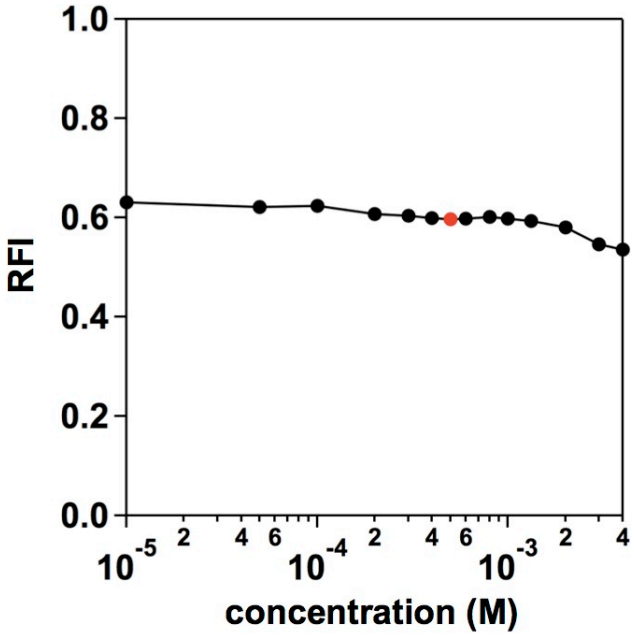

Fig. S12 Effect of concentration of *trans*-ABPX103^0 on the fluorescence intensity at 520 nm. Water content was 0.3 wt%. Maximum or stable fluorescence intensity at 520 nm was observed by the addition of more than 300 μM of *trans*-ABPX103^0. Thus, we decided to use 500 μM *trans*-ABPX103^0 (red circle) solution for all measurements.

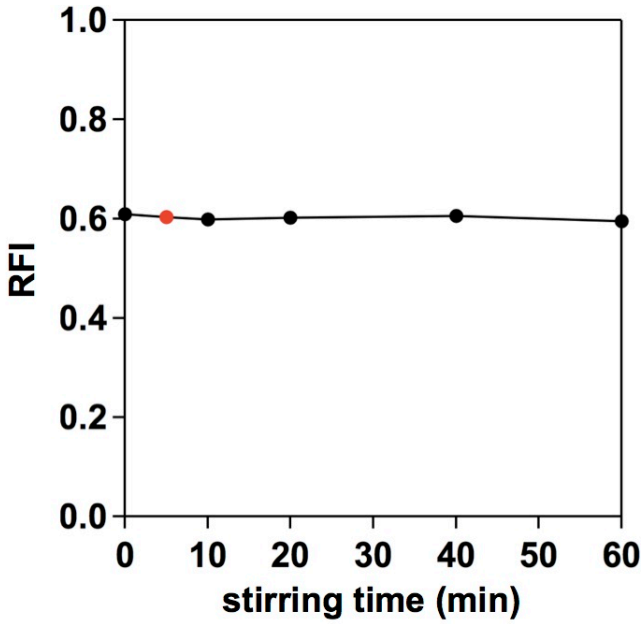

Fig. S13 Effect of the stirring time on the fluorescence at 520 nm. *trans*-ABPX103^0, 500 μM; Water content was 0.3 wt%. A 5 min stirring time (red circle) was selected for all measurements.

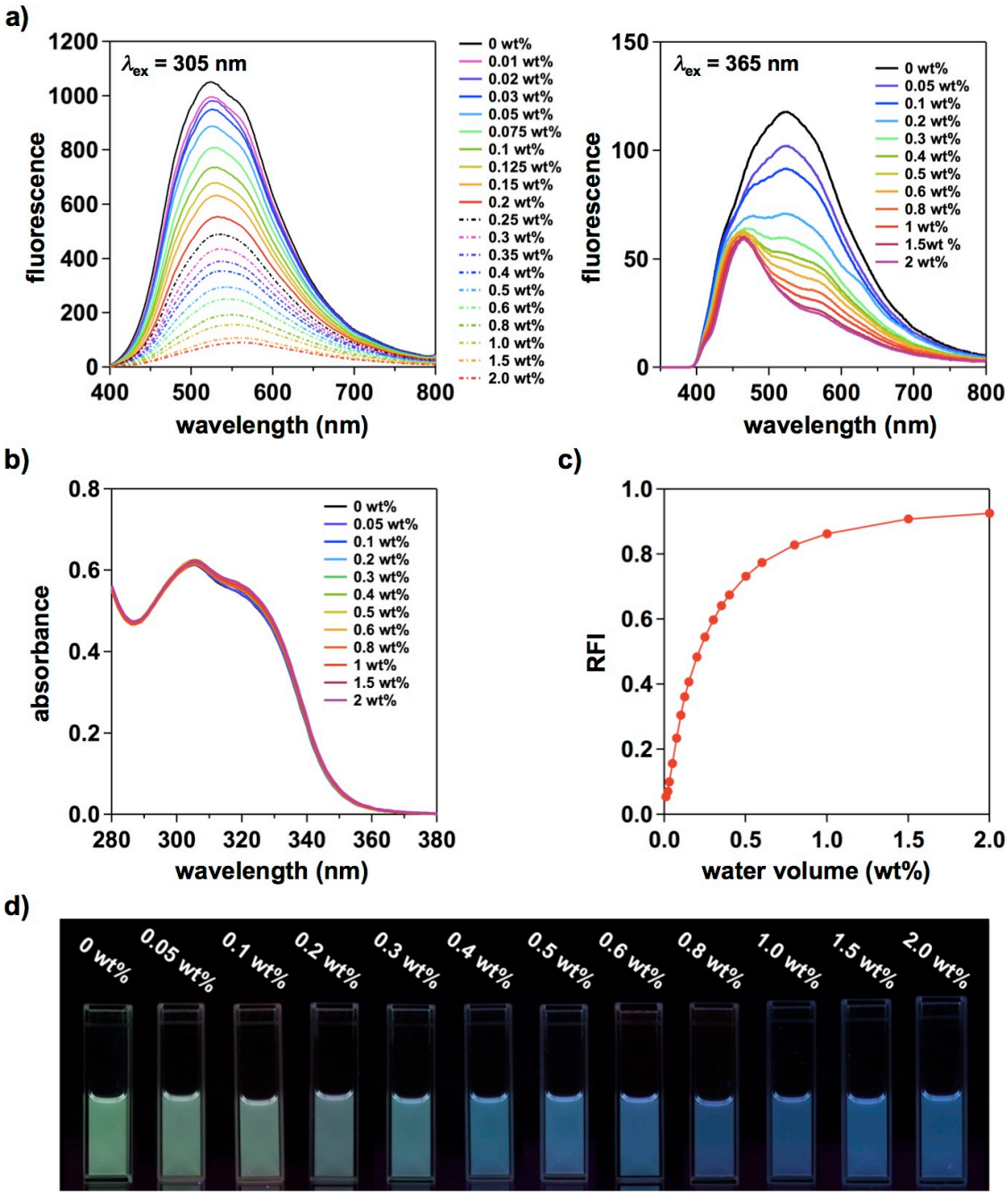

Fig. S14 a) Fluorescence (λ_{ex} = 305 nm and 365 nm) and b) absorption spectra, c) calibration curve and d) photograph (λ_{ex} = 365 nm) of *trans*-ABPX103^{0} obtained by increasing water content in dehydrated THF.

3. References

1. S. Kamino, A. Muranaka, M. Murakami, A. Tatsumi, N. Nagaoka, Y. Shirasaki, K. Watanabe, K. Yoshida, J. Horigome, S. Komeda, M. Uchiyama and S. Enomoto, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2131-2140.
2. M. Tanioka, S. Kamino, A. Muranaka, Y. Ooyama, H. Ota, Y. Shirasaki, J. Horigome, M. Ueda, M. Uchiyama, D. Sawada and S. Enomoto, *J. Am. Chem. Soc.*, 2015, **137**, 6436-6439.