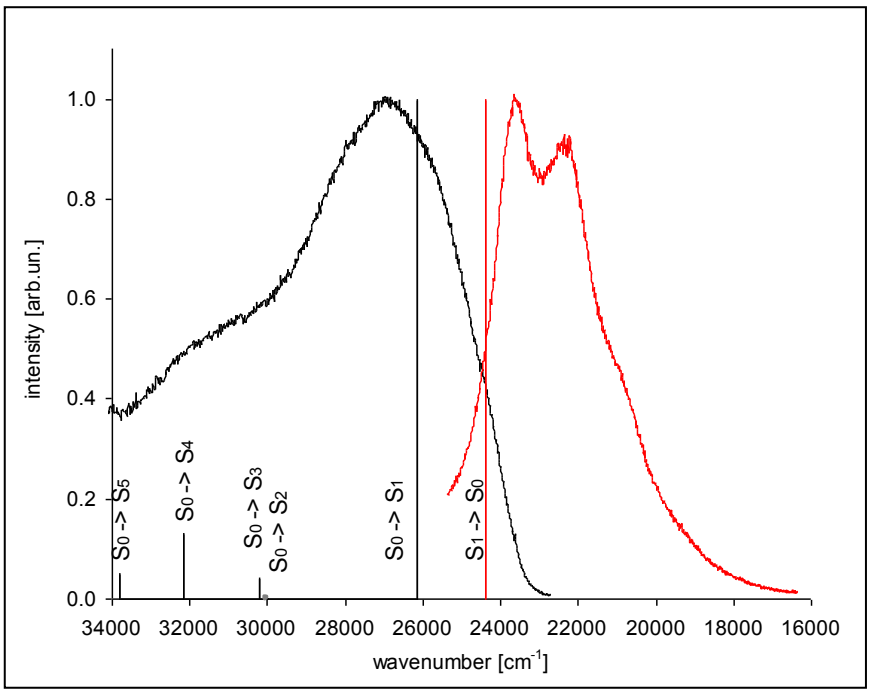


Fig.S1. Room-temperature absorption and fluorescence spectra of DPO in *iso*-octane and the TD DFT B3LYP/6-31G(d, p) calculated energies of the corresponding transitions; $S_0 \rightarrow S_i$ (absorption) and $S_1 \rightarrow S_0$ (emission) with i = 0,1…, 5.

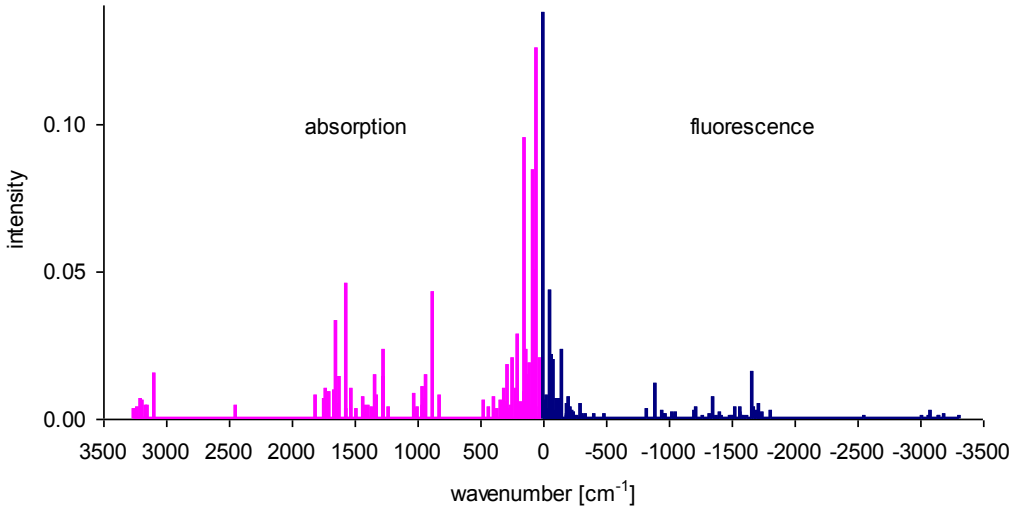


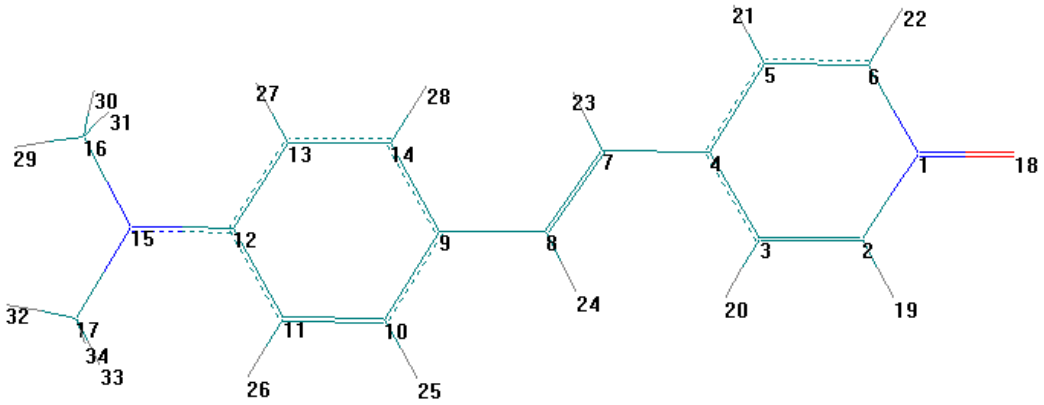
Fig.S2. The TD DFT B3LYP/6-31G(d, p) calculated lines corresponding to vibronic transitions in the absorption and fluorescence spectra of *trans*-DPO.

Table S1. The xyz coordinates and the energies of the *trans*-DPO and *cis*-DPO isomers in the DFT and TD DFT/ B3LYP/6-31G(d, p) optimized structures in the S_0 and S_1 states.

	trans-DPO						*cis*-DPO					
	S_0			S_1			S_0			S_1		
	E= -765.903071836			E= -765.8991620			E= -765.894941237			E= -765.880072504		
	x	y	z	x	y	z	x	y	z	x	y	z
7	5.6466	-0.0657	0.0160	5.6225	-0.0485	0.0003	-4.1894	-1.3223	-0.2360	-3.7769	-1.4634	-0.2508
6	4.8097	-1.1571	0.0424	4.8018	-1.1495	0.0017	-2.9457	-1.2704	-0.8206	-2.5793	-1.2339	-0.8650
6	3.4399	-1.0227	0.0330	3.4324	-1.0419	0.0014	-2.1237	-0.1731	-0.6848	-1.9144	-0.0286	-0.7551
6	2.8205	0.2452	-0.0048	2.7917	0.2460	-0.0004	-2.5181	0.9558	0.0621	-2.4707	1.0460	0.0342
6	3.7038	1.3427	-0.0302	3.6768	1.3611	-0.0016	-3.8086	0.8869	0.6213	-3.7577	0.7915	0.5872
6	5.0733	1.1801	-0.0200	5.0378	1.2132	-0.0013	-4.6090	-0.2279	0.4773	-4.3791	-0.4193	0.4526
6	1.3818	0.4655	-0.0173	1.3816	0.4301	-0.0008	-1.7323	2.1850	0.1957	-1.8049	2.2799	0.2552
6	0.4173	-0.4834	-0.0117	0.4140	-0.5704	-0.0004	-0.3975	2.4053	0.1363	-0.4503	2.5661	0.0287
6	-1.0258	-0.2837	-0.0214	-1.0051	-0.3480	-0.0002	0.7438	1.4855	0.0900	0.6423	1.6473	0.0722
6	-1.8794	-1.4025	-0.0365	-1.9009	-1.4542	-0.0017	1.9466	1.9090	-0.5044	1.9118	2.0144	-0.4568
6	-3.2616	-1.2851	-0.0458	-3.2719	-1.3008	-0.0016	3.0770	1.1050	-0.5492	2.9856	1.1532	-0.4639
6	-3.8814	-0.0140	-0.0473	-3.8630	-0.0057	-0.0001	3.0720	-0.1878	0.0245	2.8770	-0.1625	0.0886
6	-3.0286	1.1179	-0.0198	-2.9857	1.1092	0.0017	1.8801	-0.5999	0.6688	1.6462	-0.5194	0.6855
6	-1.6507	0.9796	-0.0104	-1.6130	0.9445	0.0017	0.7572	0.2139	0.6935	0.5644	0.3467	0.6852
7	-5.2585	0.1212	-0.0798	-5.2366	0.1547	-0.0003	4.1833	-1.0128	-0.0365	3.9451	-1.0335	0.0509
6	-5.8595	1.4330	0.0926	-5.8168	1.4862	0.0000	4.2046	-2.2476	0.7296	3.8254	-2.3538	0.6471
6	-6.0994	-1.0566	0.0486	-6.1120	-1.0050	0.0007	5.4424	-0.4844	-0.5334	5.2348	-0.6040	-0.4662
8	6.9157	-0.2116	0.0254	6.9051	-0.1662	0.0004	-4.9323	-2.3527	-0.3633	-4.3735	-2.5983	-0.3314
1	5.3344	-2.1023	0.0713	5.3424	-2.0872	0.0030	-2.6974	-2.1576	-1.3870	-2.2230	-2.0757	-1.4446
1	2.8490	-1.9316	0.0572	2.8487	-1.9549	0.0028	-1.1617	-0.1940	-1.1823	-1.0291	0.1330	-1.3544
1	3.3118	2.3549	-0.0593	3.2697	2.3689	-0.0029	-4.1996	1.7239	1.1919	-4.2574	1.5680	1.1601
1	5.7906	1.9892	-0.0387	5.7553	2.0216	-0.0022	-5.6004	-0.3344	0.8957	-5.3447	-0.6796	0.8623
1	1.0885	1.5135	-0.0347	1.0511	1.4669	-0.0017	-2.3464	3.0729	0.3416	-2.4346	3.1080	0.5825
1	0.7210	-1.5296	-0.0014	0.7304	-1.6097	-0.0008	-0.1069	3.4559	0.1454	-0.1846	3.6110	-0.1269
1	-1.4420	-2.3982	-0.0375	-1.4849	-2.4581	-0.0030	1.9944	2.8997	-0.9503	2.0244	3.0028	-0.8949
1	-3.8600	-2.1874	-0.0502	-3.8957	-2.1863	-0.0030	3.9698	1.4906	-1.0254	3.9190	1.4842	-0.9021
1	-3.4478	2.1162	-0.0032	-3.3856	2.1160	0.0034	1.8325	-1.5590	1.1693	1.5363	-1.4791	1.1755
1	-1.0466	1.8816	0.0121	-0.9887	1.8313	0.0036	-0.1246	-0.1370	1.2191	-0.3295	0.0760	1.2308
1	-6.9439	1.3416	0.0213	-6.9035	1.4067	-0.0031	5.1354	-2.7786	0.5257	4.7363	-2.9206	0.4550
1	-5.5346	2.1250	-0.6932	-5.5127	2.0594	-0.8863	3.3792	-2.9064	0.4373	2.9822	-2.9061	0.2149
1	-5.6171	1.8865	1.0655	-5.5176	2.0574	0.8894	4.1363	-2.0791	1.8152	3.6741	-2.3032	1.7348
1	-7.1459	-0.7597	-0.0288	-7.1496	-0.6724	0.0019	6.1869	-1.2817	-0.5399	5.9311	-1.4416	-0.4300
1	-5.9600	-1.5758	1.0089	-5.9532	-1.6315	0.8886	5.8308	0.3431	0.0800	5.6624	0.2206	0.1207
1	-5.8993	-1.7746	-0.7552	-5.9553	-1.6315	-0.8876	5.3386	-0.1223	-1.5625	5.1593	-0.2749	-1.5100

Table S2. Comparison of the chosen bondlengths in various optimized structures of the *trans*-DPO.The atom numeration on the top of the Table; *trans*-DPO-S_0- ground state optimization;

trans-DPO-S_1- excited state optimization; *trans*-DPO-S_0 in ACN- ground state optimization in acetonitrile; *trans* – DPO-S_0 cryst- crystallographic experimental data for DPO; *trans*- DPO-MeOH complex- S_0 - ground state optimization of DPO-MeOH complex.



	trans-DPO-S_0	*trans* – DPO-S_0 cryst[32(c)]	*trans*-DPO-S_0 in ACN	*trans*- DPO-MeOH complex-S_0	*trans*-DPO-S_1
N1-O18	1.278	1.301	1.292	1.296	1.288
N1-C6	1.372	1.394	1.368	1.368	1.391
C5-C4	1.409	1.400	1.410	1.409	1.424
C3-C4	1.412	1.401	1.413	1.412	1.438
C4-C7	1.455	1.447	1.455	1.455	1.422
C7-C8	1.354	1.339	1.356	1.354	1.392
C8-C9	1.457	1.447	1.456	1.456	1.436
C9-C14	1.410	1.402	1.411	1.410	1.428
C9-C10	1.407	1.402	1.410	1.407	1.423
C11-C12	1.414	1.416	1.417	1.415	1.423
C13-C12	1.417	1.401	1.421	1.418	1.419
C12-N15	1.384	1.370	1.375	1.382	1.383

Table S3. The vibration frequencies of *trans*-DPO structures optimized in the S_0 and S_1 state. The bold numbers indicate the vibrations with the large FC factor both in the absorption and emission.

S_0		S_1	
zero-point correction	0.2804 H	zero-point correction	0.2767 H
frequency	red.mass	frequency	red.mass

	hν	μ	hν	μ
1	13.8	3.3347	20.8	3.4270
2	**30.2**	**5.2854**	26.3	5.1340
3	**52.6**	**5.2821**	**53.1**	**5.3114**
4	**61.9**	**4.0067**	56.3	2.4709
5	69.7	2.5762	**64.3**	**4.5666**
6	**77.8**	**2.3329**	85.5	2.1246
7	141.5	1.8435	132.8	2.5895
8	**154.4**	**4.6070**	**153.1**	**5.8184**
9	179.4	3.3908	197.4	1.8213
10	187.7	1.6048	203.2	1.4273
11	218.4	2.3984	206.2	4.7742
12	238.7	2.1378	239.9	2.0529
13	290.9	3.3732	285.3	4.0659
14	341.8	3.6596	324.7	3.2102
15	398.0	4.7693	358.5	4.3983
16	403.1	3.7214	395.2	4.1212
17	425.9	3.2365	404.5	3.1177
18	429.7	3.3639	419.8	3.2312
19	432.9	4.9430	422.5	5.2066
20	486.6	4.3649	460.0	2.3392
21	512.9	3.2923	478.9	4.4712
22	515.5	3.9082	509.0	4.3775
23	519.9	2.9566	510.0	3.8686
24	549.9	2.2668	516.4	2.2287
25	593.2	5.0335	584.5	4.8376
26	654.9	7.1342	640.4	7.1971
27	676.8	7.0252	664.8	4.1474
28	715.1	3.7023	664.8	6.0842
29	738.3	4.4243	711.3	3.5989
30	740.5	4.6445	728.6	4.7564
31	810.7	1.2785	738.8	1.5361
32	819.1	1.4618	756.3	1.7811
33	824.2	1.4683	777.0	1.3639
34	830.2	5.0703	778.4	1.3590
35	843.6	1.7370	819.2	2.1417
36	866.0	5.6581	819.4	3.5230
37	878.6	1.9813	839.6	6.1533
38	**896.3**	**4.5493**	853.0	1.2741
39	938.5	1.2811	**875.1**	**4.3063**
40	943.0	1.3176	897.4	1.2529
41	947.5	1.3132	916.8	1.2976
42	950.3	1.3481	928.6	1.2907
43	970.1	3.1496	946.6	1.3021
44	997.8	1.1261	958.8	3.3074
45	1021.2	2.7494	1001.5	2.7322
46	1042.0	2.6463	1011.4	2.9470
47	1085.4	1.5158	1084.8	1.5351
48	1117.5	1.4837	1107.0	1.5137
49	1143.4	1.3199	1133.7	1.2345
50	1146.8	1.2433	1135.9	1.3192

51	1162.9	1.5033	1157.0	1.6049
52	1200.1	1.1893	1181.5	1.3395
53	1202.2	1.6944	1182.0	1.5935
54	1218.1	1.4489	1215.0	1.6402
55	1238.2	1.6960	1232.3	1.6540
56	1257.7	1.7985	1251.8	1.7809
57	1280.5	3.2451	1264.0	2.2328
58	1285.1	2.6007	**1270.4**	**3.0944**
59	1322.1	2.0253	1275.8	2.0338
60	1337.8	1.6745	1317.6	2.3263
61	**1356.7**	**1.6068**	1332.2	3.9506
62	1367.3	3.4573	1338.2	1.8746
63	1373.3	1.8868	1371.4	2.2953
64	1383.9	2.7033	1377.0	2.1915
65	1394.8	3.3239	1393.1	3.6602
66	1455.8	1.2317	1431.2	2.6398
67	1482.4	2.4845	1453.1	1.2107
68	1493.4	1.0480	1476.8	2.1926
69	1497.8	3.0575	1484.8	1.0387
70	1500.1	1.1448	1490.3	1.2842
71	1502.4	1.1533	1495.3	1.0454
72	1524.9	2.5548	1497.7	2.3817
73	1528.5	1.1029	1520.8	2.2981
74	1543.3	1.0863	1524.9	1.6068
75	1563.8	5.6825	1534.0	2.9553
76	1571.7	2.6615	1537.5	1.3439
77	1598.0	5.6875	1541.6	1.6442
78	**1658.7**	**4.8860**	**1572.2**	**2.9992**
79	1682.3	5.5662	1642.0	5.2477
80	1696.2	5.3035	**1654.1**	**5.5125**
81	2995.1	1.0467	3005.0	1.0377
82	3002.8	1.0507	3014.2	1.0408
83	3062.8	1.0926	3052.1	1.1036
84	3064.1	1.0942	3055.1	1.1043
85	3139.2	1.0979	3149.8	1.0978
86	3145.9	1.0888	3159.3	1.0864
87	3150.5	1.0954	3162.6	1.0951
88	3159.4	1.0864	3178.1	1.0864
89	3174.1	1.0891	3184.0	1.0884
90	3189.1	1.0880	3185.0	1.0893
91	3198.3	1.0902	3201.3	1.0865
92	3210.0	1.0896	3213.6	1.0867
93	3226.3	1.0911	3224.8	1.0920
94	3227.9	1.0908	3226.7	1.0912
95	3259.8	1.0938	3249.9	1.0945
96	3261.5	1.0947	3263.8	1.0930

Table S4. Comparison of the energy and oscillator strength for the $S_0 \rightarrow S_i$ electronic transitions in *trans*-DPO and *trans*-DPO…MeOH complex.

	trans-DPO		*trans*-DPO…MeOH	
	ΔE(So→Si) [cm^{-1}]	Oscillator strength	ΔE(S_0→S_i) [cm^{-1}]	Oscillator strength
S_1	26145	1.1818	25661	1.2048
S_2	30016	0.0000	30565	0.0196
S_3	30209	0.0405	31376	0.0005
S_4	32161	0.1322	32517	0.1897
S_5	33820	0.0494	33509	0.0011
S_6	37404	0.0029	34146	0.0414
S_7	38927	0.0209	37528	0.0030
S_8	39410	0.0000	38499	0.0328
S_9	39591	0.0120	39530	0.0118

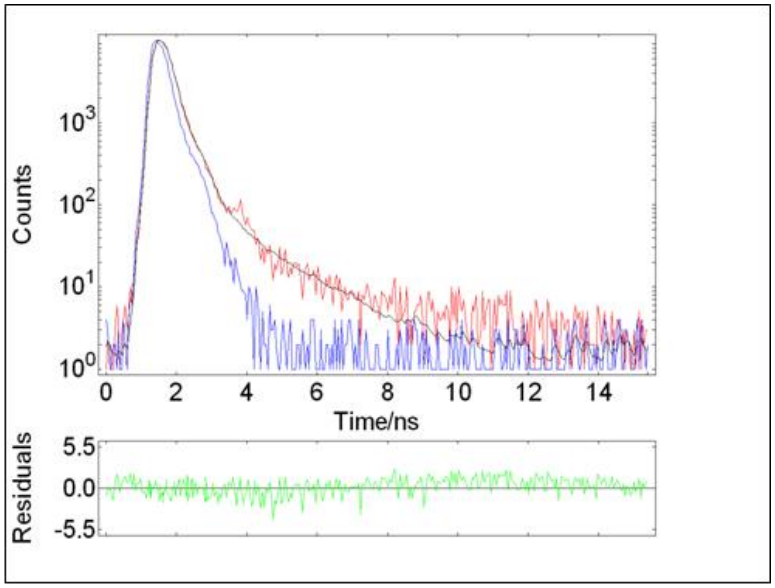


Fig. S3. The fluorescence decay curve of *trans*-DPO in 1,4-dioxane (exc = 375 nm, em = 464 nm).

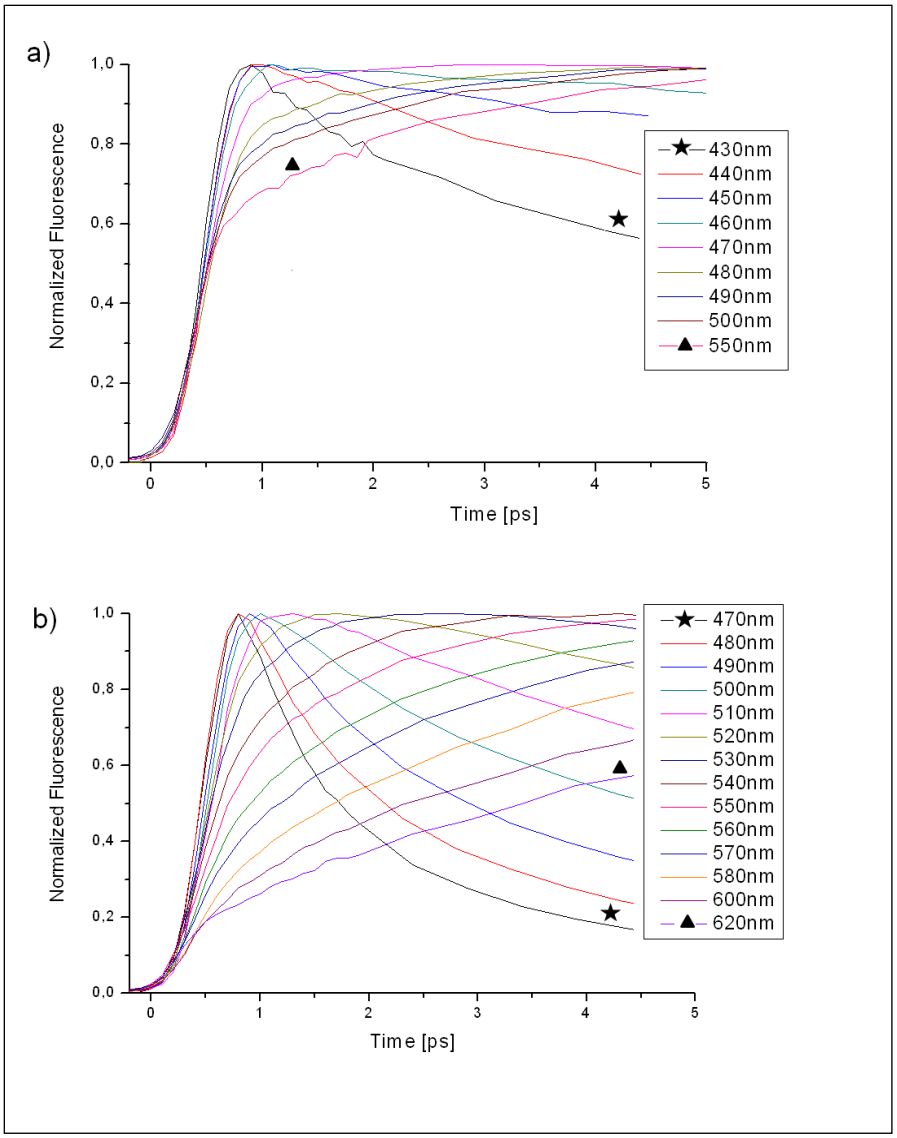


Fig. S4. The up-conversion signals of *trans*-DPO in (a) dioxane , (b) methanol, probed at different wavelengths.