Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Charge transfer states in triazole linked donor-acceptor materials: strong effects of chemical modifications and solvation

Electronic Supplementary Information

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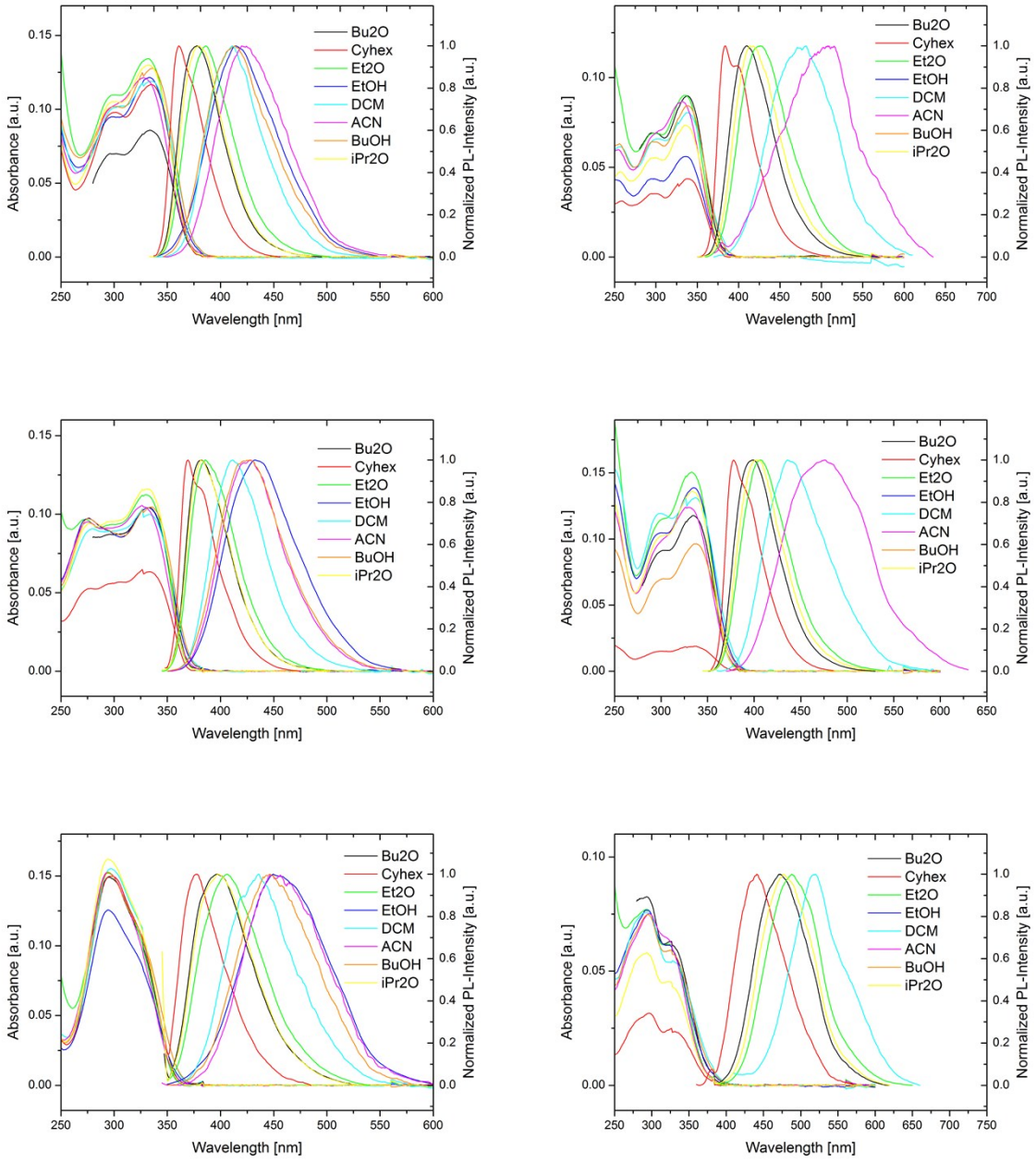

Figure S1. UV/VIS absorption and photoluminescence emission spectra of **ZMSOM-14TPA** (top left), **ZMSO$_2$M-14TPA** (top right), **EMSM-14TPA** (middle left), **EMSO$_2$M-14TPA** (middle right), **ZMSM-15TPA** (bottom left) and **ZMSO$_2$M-15TPA** (bottom right) in various solvents (Cyhex=cyclohexane, DCM=dichloromethane, ACN=acetonitrile).

Table S1. UV/Vis Absorption and fluorescence maxima of the materials in various solvents (Cyhex=cyclohexane, DCM=dichloromethane, ACN=acetonitrile).

		Cyhex	Bu2O	iPr2O	Et2O	DCM	BuOH	EtOH	ACN
ZMSM-14TPA	Abs	333.5	333	332	331.5	333.5	335.5	333	328
	Em	368.5	380.5	381.5	389	410.5	427	432.5	424.5
ZMSOM-14TPA	Abs	335	334	332.5	332	335.5	336	333	328
	Em	376.5	396.5	399	405.5	434	436.5	437	444
$ZMSO_2M$-14TPA	Abs	338	338	336	335.5	338.5	338	336	332
	Em	384	410	413.5	426	481	---	---	507.5
EMSM-14TPA	Abs	333	332.5	331.5	329.5	333	335	332	326.5
	Em	369.5	382	381.5	386	411.5	427	432.5	428
$EMSO_2M$-14TPA	Abs	337	335	333.5	333	337	337	335	330
	Em	378	398.5	402.5	406.5	435.5	---	---	475.5
ZMSM-15TPA	Abs	325.5	329.5	324	294.5	297	324.5	325.5	324
	Em	378	397.5	398.5	406	436	446.5	449.5	446.5
$ZMSO_2M$-15TPA	Abs	331	325.5	323	293.5	266	325.5	323.5	320
	Em	441	472	477	488	519.5	---	---	---

Table S2. Atomic coordinates (Å) and total energies (a.u.) of **ZMSM-14TPA** optimized in the S_0 and S_1 states.

S_0				S_1			
DFT/ωPBEh energy: -1543.530381578				TDDFT/ωPBEh energy: -1543.401686816			
C	-6.99377	-2.50970	0.94822	C	-6.81471	-0.82237	2.71022
S	-5.78968	-1.52798	0.01427	S	-5.83671	-1.16936	1.21991
H	-6.53076	-3.49265	1.08428	H	-6.36230	-1.41186	3.51494
H	-7.93255	-2.64212	0.40163	H	-7.85961	-1.13075	2.60159
H	-7.18873	-2.07601	1.93452	H	-6.76291	0.23831	2.97882
C	-6.56499	0.05912	-0.11629	C	-6.56352	-0.08200	0.02116
C	-8.06451	0.10392	-0.19274	C	-8.06451	-0.04618	-0.04805
H	-8.44162	-0.52682	-1.00981	H	-8.48188	-1.05666	-0.16495
H	-8.40075	1.13191	-0.36836	H	-8.39188	0.56438	-0.89778
H	-8.53462	-0.24466	0.73662	H	-8.51039	0.38716	0.85864
C	-5.82493	1.18296	-0.23672	C	-5.80163	0.60159	-0.86527
C	-4.38803	1.36835	-0.18999	C	-4.36871	0.72946	-0.99651
H	-6.36306	2.11742	-0.39708	H	-6.33336	1.16349	-1.63513
C	-3.30621	0.50709	-0.11096	C	-3.27848	0.21120	-0.30099
N	-2.22142	1.32103	-0.10819	N	-2.18617	0.73887	-0.93063
N	-2.59549	2.61480	-0.18883	N	-2.58816	1.53924	-1.97065
N	-3.88685	2.64621	-0.24004	N	-3.88593	1.52404	-1.99725
C	-0.85198	0.96378	-0.05240	C	-0.84246	0.55717	-0.65922
H	-3.22268	-0.56850	-0.09607	H	-3.21522	-0.44294	0.55197
C	-0.45099	-0.18167	0.63640	C	-0.42132	-0.31842	0.38812
C	0.09790	1.76113	-0.69302	C	0.13259	1.23504	-1.43647
C	0.89208	-0.53773	0.67009	C	0.92358	-0.49932	0.63423
C	1.43886	1.40000	-0.66072	C	1.47432	1.05910	-1.18210
C	1.85718	0.24249	0.01492	C	1.88619	0.18621	-0.13527
H	-0.22485	2.65112	-1.22666	H	-0.20085	1.89344	-2.23291
H	-1.18139	-0.78198	1.17531	H	-1.14901	-0.85408	0.99053
H	1.20081	-1.42593	1.21665	H	1.24420	-1.17181	1.42893
N	3.21478	-0.13346	0.03514	N	3.28084	-0.05901	0.07173
H	2.17291	2.01489	-1.17657	H	2.21921	1.57253	-1.78781
C	3.57321	-1.50143	-0.06034	C	3.76262	-1.35625	-0.12666
C	4.23078	0.85130	0.10713	C	4.10725	0.99820	0.43426
C	5.37599	0.74424	-0.69378	C	5.47794	1.01680	0.08228
C	4.10807	1.93922	0.98288	C	3.54648	2.11498	1.09627
C	5.10912	2.90591	1.04325	C	4.35472	3.18670	1.44474
C	6.38028	1.70596	-0.61360	C	6.26530	2.10305	0.42773
C	6.25217	2.79438	0.25028	C	5.71410	3.18876	1.11926
H	3.22435	2.02350	1.61265	H	2.48690	2.10673	1.33442
H	5.47432	-0.09768	-1.37619	H	5.89634	0.19807	-0.49733
H	7.26400	1.60840	-1.24221	H	7.31402	2.11699	0.13818
H	4.99850	3.74603	1.72707	H	3.91885	4.03381	1.96993
H	7.03512	3.54817	0.30569	H	6.33796	4.03988	1.38364
C	2.91765	-2.34795	-0.96541	C	3.12642	-2.18820	-1.07230
C	4.59402	-2.02238	0.74684	C	4.81387	-1.87521	0.66149
C	4.95374	-3.36403	0.64294	C	5.23752	-3.18291	0.47191
C	3.27153	-3.69252	-1.04992	C	3.57511	-3.48729	-1.25940
C	4.29282	-4.20833	-0.25064	C	4.63119	-3.99232	-0.49432
H	2.13089	-1.94481	-1.59997	H	2.29979	-1.79052	-1.65449
H	2.75356	-4.33753	-1.75800	H	3.09296	-4.11476	-2.00586
H	5.10370	-1.36804	1.45128	H	5.25527	-1.26078	1.44256
H	4.57172	-5.25766	-0.32445	H	4.96748	-5.01724	-0.63564
H	5.74893	-3.75423	1.27619	H	6.03450	-3.58229	1.09605

Table S3. Atomic coordinates (Å) and total energies (a.u.) of **ZMOSM-14TPA** optimized in the S_0 and S_1 states.

S_0				S_1			
DFT/ωPBEh energy: -1618.635052378				TDDFT/ωPBEh energy: -1618.508807511			
C	-5.71624	-1.15923	2.05737	C	5.49309	-0.53194	2.36861
S	-6.00636	-1.57998	0.30838	S	5.92271	0.96592	1.42164
H	-5.40438	-2.07951	2.56210	H	5.14392	-0.20211	3.35307
H	-6.64676	-0.78804	2.50099	H	6.38679	-1.15660	2.47695
H	-4.92993	-0.40103	2.12659	H	4.70202	-1.08165	1.84854
C	-6.49471	0.09247	-0.21227	C	6.44385	0.13274	-0.09361
C	-7.98768	0.18461	-0.36342	C	7.93751	0.20684	-0.26251
H	-8.35103	-0.47652	-1.16229	H	8.28360	1.24388	-0.38043
H	-8.28695	1.21134	-0.60171	H	8.24789	-0.35825	-1.14923
H	-8.51143	-0.11309	0.55707	H	8.47514	-0.20935	0.60313
C	-5.67512	1.13079	-0.46198	C	5.64140	-0.48525	-0.99476
C	-4.23668	1.30786	-0.39313	C	4.21712	-0.67133	-1.08080
H	-6.16950	2.05750	-0.76361	H	6.15451	-0.95073	-1.83997
C	-3.15484	0.45369	-0.26921	C	3.12470	-0.16569	-0.37782
N	-2.07819	1.27044	-0.29672	N	2.04010	-0.73207	-0.98542
N	-2.45722	2.56334	-0.43285	N	2.45230	-1.55741	-2.01156
N	-3.74610	2.58672	-0.49583	N	3.74245	-1.50491	-2.05852
C	-0.70442	0.92831	-0.21481	C	0.69835	-0.56381	-0.71183
H	-3.11872	-0.62739	-0.22859	H	3.08884	0.59076	0.39310
C	-0.30836	-0.24506	0.42761	C	0.28282	0.28212	0.35996
C	0.25292	1.77326	-0.77881	C	-0.27787	-1.22176	-1.50337
C	1.03957	-0.57444	0.50093	C	-1.06209	0.46143	0.61048
C	1.59871	1.43743	-0.70851	C	-1.61919	-1.04350	-1.24427
C	2.01475	0.25904	-0.06834	C	-2.02527	-0.19373	-0.18042
H	-0.06601	2.68174	-1.28219	H	0.05178	-1.86174	-2.31617
H	-1.04600	-0.89478	0.89363	H	1.01581	0.79454	0.97595
H	1.34354	-1.48507	1.01183	H	-1.37985	1.11127	1.42487
N	3.37758	-0.08833	-0.00100	N	-3.41973	0.05079	0.03618
H	2.33884	2.09146	-1.16368	H	-2.36709	-1.53711	-1.86261
C	3.76542	-1.44885	-0.10934	C	-3.89643	1.35429	-0.11680
C	4.37204	0.90736	0.15851	C	-4.24776	-1.01686	0.36754
C	5.57464	0.82171	-0.55656	C	-5.61365	-1.02969	-0.00086
C	4.17568	1.98247	1.03700	C	-3.69179	-2.14592	1.01106
C	5.16074	2.95636	1.18384	C	-4.50108	-3.22757	1.32503
C	6.56140	1.79000	-0.38928	C	-6.40223	-2.12589	0.30959
C	6.36048	2.86574	0.47666	C	-5.85623	-3.22562	0.98235
H	3.24877	2.05042	1.60310	H	-2.63545	-2.14090	1.26352
H	5.73137	-0.00934	-1.24100	H	-6.02704	-0.19837	-0.56616
H	7.48969	1.70776	-0.95236	H	-7.44718	-2.13594	0.00669
H	4.99172	3.78537	1.86925	H	-4.06949	-4.08508	1.83662
H	7.13032	3.62488	0.59983	H	-6.48073	-4.08429	1.21932
C	3.20544	-2.27055	-1.09660	C	-3.24888	2.22173	-1.02301
C	4.71863	-1.98276	0.76789	C	-4.95745	1.84304	0.67830
C	5.10742	-3.31536	0.65229	C	-5.37711	3.15747	0.53565
C	3.58693	-3.60673	-1.19449	C	-3.69326	3.52795	-1.16289
C	4.54163	-4.13590	-0.32468	C	-4.75732	4.00356	-0.39025
H	2.47053	-1.85527	-1.78336	H	-2.41709	1.84594	-1.61209
H	3.14355	-4.23381	-1.96625	H	-3.20130	4.18434	-1.87727
H	5.15351	-1.34514	1.53509	H	-5.40702	1.19935	1.43032
H	4.84258	-5.17835	-0.40833	H	-5.08987	5.03414	-0.49404
H	5.84984	-3.71718	1.33991	H	-6.18019	3.53377	1.16607
O	-4.66553	-1.99559	-0.26493	O	4.62695	1.74487	1.25707

Table S4. Atomic coordinates (Å) and total energies (a.u.) of **ZMSO$_2$M-14TPA** optimized in the S_0 and S_1 states.

S_0				S_1			
DFT/ωPBEh energy: -1693.780560428				TDDFT/ωPBEh energy: -1693.657570335			
C	-5.38994	-0.89746	2.00909	C	5.11098	-1.09464	1.98682
S	-5.78399	-1.24907	0.29537	S	5.71772	0.47302	1.35474
H	-5.11353	-1.85520	2.46242	H	4.79717	-0.91031	3.01971
H	-6.27846	-0.48920	2.49870	H	5.92660	-1.82238	1.95960
H	-4.55443	-0.19312	2.05681	H	4.26436	-1.42765	1.37906
C	-6.25100	0.35485	-0.37014	C	6.23539	0.10220	-0.30923
C	-7.71924	0.48620	-0.65281	C	7.72244	0.17271	-0.51793
H	-8.05161	-0.26668	-1.37738	H	8.11105	1.17763	-0.31146
H	-7.92917	1.48231	-1.05766	H	7.95452	-0.08212	-1.55843
H	-8.32415	0.33860	0.25091	H	8.26800	-0.51508	0.14134
C	-5.37469	1.36252	-0.54975	C	5.37394	-0.27727	-1.28788
C	-3.93974	1.49804	-0.37319	C	3.94397	-0.41389	-1.36708
H	-5.81405	2.30495	-0.88414	H	5.84533	-0.56297	-2.23073
C	-2.87415	0.61778	-0.28143	C	2.86636	-0.02794	-0.56685
N	-1.78626	1.41428	-0.19341	N	1.76409	-0.46903	-1.24510
N	-2.14072	2.71943	-0.23282	N	2.15110	-1.10202	-2.40813
N	-3.42501	2.77150	-0.34888	N	3.44023	-1.05354	-2.46800
C	-0.42105	1.03613	-0.11163	C	0.42890	-0.34556	-0.92336
H	-2.83232	-0.46003	-0.33467	H	2.83375	0.57068	0.32917
C	-0.05954	-0.16157	0.50553	C	0.03098	0.33371	0.26616
C	0.55906	1.86445	-0.65978	C	-0.56151	-0.89545	-1.77865
C	1.27661	-0.53746	0.56053	C	-1.30975	0.45512	0.57230
C	1.89358	1.48401	-0.60682	C	-1.89707	-0.77940	-1.46149
C	2.27510	0.27454	-0.00214	C	-2.28251	-0.09638	-0.28009
H	0.26676	2.79353	-1.14168	H	-0.24695	-1.41085	-2.68095
H	-0.81538	-0.79465	0.96573	H	0.77163	0.77290	0.92784
H	1.55395	-1.46791	1.05013	H	-1.61388	0.97986	1.47711
N	3.62218	-0.12422	0.03569	N	-3.67712	0.04288	0.03671
H	2.65102	2.12391	-1.05292	H	-2.65492	-1.20135	-2.11950
C	3.96059	-1.49703	-0.09266	C	-4.24901	1.31459	-0.00636
C	4.66036	0.83570	0.13786	C	-4.40627	-1.09392	0.36701
C	5.80604	0.72093	-0.66056	C	-5.79165	-1.18316	0.09142
C	4.56064	1.90110	1.04337	C	-3.73424	-2.21022	0.91553
C	5.58457	2.84117	1.13325	C	-4.44754	-3.35605	1.23178
C	6.83315	1.65535	-0.55115	C	-6.48332	-2.34347	0.39919
C	6.72744	2.72311	0.34086	C	-5.82116	-3.43074	0.98120
H	3.67717	1.98888	1.67308	H	-2.66537	-2.14580	1.09564
H	5.88677	-0.10498	-1.36443	H	-6.29580	-0.35925	-0.40678
H	7.71721	1.55271	-1.17833	H	-7.54339	-2.41276	0.16458
H	5.49251	3.66445	1.83984	H	-3.92682	-4.20327	1.67214
H	7.52817	3.45582	0.41924	H	-6.37064	-4.33911	1.21816
C	3.34375	-2.29356	-1.06660	C	-3.71877	2.28106	-0.88831
C	4.92508	-2.06542	0.74937	C	-5.29232	1.67526	0.87660
C	5.26720	-3.40906	0.61392	C	-5.81096	2.96099	0.84320
C	3.67869	-3.64060	-1.18382	C	-4.26345	3.55563	-0.92047
C	4.64325	-4.20509	-0.34793	C	-5.31037	3.90359	-0.06053
H	2.60154	-1.85109	-1.72818	H	-2.89666	2.00573	-1.54257
H	3.19129	-4.24847	-1.94434	H	-3.86319	4.28852	-1.61731
H	5.40507	-1.44622	1.50480	H	-5.64830	0.95907	1.61310
H	4.90742	-5.25617	-0.44631	H	-5.72023	4.91101	-0.07957
H	6.01887	-3.83852	1.27419	H	-6.59692	3.23904	1.54224
O	-6.98682	-2.08949	0.28351	O	6.92629	0.80919	2.12380
O	-4.55400	-1.73632	-0.35053	O	4.57877	1.40975	1.36939

Table S5. Atomic coordinates (Å) and total energies (a.u.) of **EMSM-14TPA** optimized in the S_0 and S_1 states.

S_0				S_1			
DFT/ωPBEh energy: -1543.530552918				TDDFT/ωPBEh energy: -1543.401988595			
C	5.57777	-2.01658	-0.06338	C	-5.54847	-1.30000	1.65107
C	6.33000	-0.71327	-0.02251	C	-6.28831	-0.45802	0.64581
S	8.07347	-0.96496	-0.03247	S	-8.03664	-0.59260	0.84672
C	5.74049	0.50091	0.01614	C	-5.69076	0.30792	-0.29594
C	4.31867	0.78855	0.02310	C	-4.27364	0.47923	-0.52885
H	6.34342	1.40499	0.04952	H	-6.29313	0.88664	-0.99264
C	3.17239	0.01064	-0.02337	C	-3.12404	-0.00913	0.09097
N	2.14898	0.90215	0.02569	N	-2.08868	0.53528	-0.61958
N	2.61987	2.16147	0.09735	N	-2.58100	1.31965	-1.62988
N	3.91209	2.09871	0.09701	N	-3.87921	1.27936	-1.56234
C	0.75480	0.65196	0.00850	C	-0.72521	0.38891	-0.44180
H	2.99793	-1.05366	-0.05020	H	-2.96849	-0.65149	0.94134
C	0.24213	-0.44544	-0.68405	C	-0.20661	-0.44686	0.59269
C	-0.11045	1.51418	0.68404	C	0.17368	1.07476	-1.30280
C	-1.12686	-0.68540	-0.69353	C	1.15687	-0.58025	0.75248
C	-1.47747	1.27002	0.67609	C	1.53345	0.94307	-1.13689
C	-2.00912	0.16585	-0.01036	C	2.04352	0.11135	-0.10091
H	0.29765	2.36539	1.22238	H	-0.23425	1.70154	-2.08974
H	0.90508	-1.09696	-1.24990	H	-0.87432	-0.98663	1.25784
H	-1.52040	-1.53464	-1.24723	H	1.55269	-1.21554	1.54356
N	-3.39383	-0.08382	-0.01619	N	3.45619	-0.05102	0.04548
H	-2.14405	1.93751	1.21722	H	2.22011	1.46175	-1.80361
C	-3.87983	-1.41587	-0.00399	C	4.00040	-1.33129	-0.08550
C	-4.32069	0.98902	-0.01592	C	4.24125	1.07164	0.29419
C	-5.45220	0.93784	0.80901	C	5.57989	1.14668	-0.15681
C	-4.12547	2.10464	-0.84171	C	3.66218	2.19067	0.93483
C	-5.04303	3.15280	-0.82992	C	4.42616	3.32576	1.16410
C	-6.37383	1.98192	0.80096	C	6.32230	2.29463	0.07007
C	-6.17356	3.09709	-0.01355	C	5.75636	3.38633	0.73960
H	-3.25192	2.14585	-1.48963	H	2.62503	2.13724	1.25281
H	-5.60550	0.07352	1.45219	H	6.00648	0.31881	-0.71749
H	-7.24862	1.92718	1.44692	H	7.34580	2.35031	-0.29516
H	-4.87735	4.01365	-1.47565	H	3.97719	4.17546	1.67397
H	-6.89145	3.91490	-0.01293	H	6.34455	4.28537	0.91084
C	-3.32526	-2.37061	0.85914	C	3.35987	-2.27094	-0.92151
C	-4.93214	-1.78883	-0.85075	C	5.12637	-1.72695	0.67106
C	-5.42271	-3.09223	-0.82714	C	5.61657	-3.01948	0.55541
C	-3.81026	-3.67649	0.86433	C	3.87409	-3.55457	-1.03564
C	-4.86329	-4.04472	0.02559	C	5.00297	-3.93690	-0.30417
H	-2.51458	-2.08281	1.52591	H	2.47754	-1.96632	-1.47745
H	-3.37044	-4.40663	1.54186	H	3.38686	-4.26647	-1.69851
H	-5.36475	-1.05000	-1.52249	H	5.57594	-1.02760	1.37177
H	-5.24514	-5.06363	0.03781	H	5.39154	-4.94962	-0.38829
H	-6.24171	-3.36656	-1.49008	H	6.47294	-3.32230	1.15470
C	8.75334	0.70508	0.00229	C	-8.70531	0.48509	-0.43487
H	6.25575	-2.87758	-0.06835	H	-6.23606	-1.86829	2.28825
H	4.95551	-2.07979	-0.96695	H	-4.92875	-0.67360	2.30756
H	4.92195	-2.11606	0.81244	H	-4.88989	-2.02017	1.14670
H	8.46685	1.23614	0.91700	H	-8.41425	0.14577	-1.43549
H	8.44418	1.28098	-0.87722	H	-8.38878	1.52415	-0.28874
H	9.84212	0.59152	-0.01406	H	-9.79513	0.43005	-0.34477

Table S6. Atomic coordinates (Å) and total energies (a.u.) of **EMSO$_2$M-14TPA** optimized in the S_0 and S_1 states.

S_0				S_1			
DFT/ωPBEh energy: -1693.782324261				TDDFT/ωPBEh energy: -1693.659700516			
C	5.07147	-1.73852	-0.00121	C	-5.05703	-0.52678	1.76950
C	5.71383	-0.38524	0.04591	C	-5.69330	-0.17884	0.45550
S	7.50359	-0.35708	0.13703	S	-7.46945	-0.22744	0.40397
C	5.10427	0.81311	0.06993	C	-5.06659	0.14564	-0.69790
C	3.67971	1.06648	0.04351	C	-3.65050	0.23796	-0.92792
H	5.72250	1.70925	0.12588	H	-5.67776	0.35902	-1.57479
C	2.56734	0.23874	0.01516	C	-2.52951	0.01846	-0.12074
N	1.51362	1.08554	0.01436	N	-1.46418	0.27494	-0.93548
N	1.93540	2.37028	0.04167	N	-1.91432	0.63762	-2.18587
N	3.22575	2.36069	0.06129	N	-3.20874	0.61054	-2.16339
C	0.12857	0.77876	-0.00155	C	-0.11061	0.20718	-0.67071
H	2.44048	-0.83304	0.03153	H	-2.41955	-0.27104	0.91079
C	-0.33538	-0.35346	-0.67135	C	0.36704	-0.24039	0.59800
C	-0.77112	1.61962	0.65483	C	0.82431	0.58201	-1.67305
C	-1.69222	-0.65239	-0.67411	C	1.72415	-0.31111	0.83908
C	-2.12624	1.31807	0.65201	C	2.17649	0.52176	-1.42326
C	-2.61116	0.17606	-0.00861	C	2.63970	0.07018	-0.15932
H	-0.40066	2.49871	1.17552	H	0.45207	0.92402	-2.63384
H	0.35456	-0.98790	-1.22476	H	-0.32547	-0.55243	1.37455
H	-2.04855	-1.52876	-1.21020	H	2.08637	-0.66790	1.80250
N	-3.98140	-0.12936	-0.00747	N	4.05465	-0.02389	0.08555
H	-2.82041	1.96911	1.17806	H	2.88869	0.81519	-2.19275
C	-4.41865	-1.47927	-0.00453	C	4.64835	-1.28564	0.10125
C	-4.95164	0.90662	-0.00902	C	4.78137	1.14567	0.27950
C	-6.06115	0.82847	0.84237	C	6.14646	1.23199	-0.08497
C	-4.82062	2.00625	-0.86754	C	4.12081	2.29391	0.77323
C	-5.77989	3.01645	-0.86076	C	4.82996	3.47016	0.95672
C	-7.02498	1.83405	0.82994	C	6.83318	2.42298	0.08749
C	-6.88805	2.93505	-0.01637	C	6.18579	3.54302	0.62084
H	-3.96490	2.06526	-1.53774	H	3.06409	2.23073	1.01374
H	-6.16448	-0.02575	1.50883	H	6.63499	0.37995	-0.55000
H	-7.88287	1.76064	1.49630	H	7.87539	2.48916	-0.21722
H	-5.66536	3.86631	-1.53159	H	4.31987	4.34333	1.35682
H	-7.63896	3.72267	-0.01903	H	6.73083	4.47524	0.75162
C	-3.83450	-2.41705	0.85746	C	4.06845	-2.32967	-0.65265
C	-5.45463	-1.88359	-0.85659	C	5.76793	-1.55778	0.92122
C	-5.89938	-3.20362	-0.84092	C	6.31110	-2.83345	0.94665
C	-4.27349	-3.73919	0.85467	C	4.63855	-3.59274	-0.63046
C	-5.30948	-4.13972	0.00932	C	5.76081	-3.85280	0.16324
H	-3.03846	-2.10326	1.53019	H	3.18759	-2.12216	-1.25273
H	-3.81197	-4.45677	1.53115	H	4.19974	-4.38582	-1.23154
H	-5.91092	-1.15660	-1.52564	H	6.16442	-0.78034	1.56941
H	-5.65556	-5.17140	0.01560	H	6.19159	-4.85131	0.18839
H	-6.70632	-3.50347	-1.50754	H	7.15684	-3.04208	1.59840
C	8.02410	-0.80266	-1.52186	C	-7.97709	1.26176	1.27364
H	5.81766	-2.53794	0.04591	H	-5.80974	-0.78664	2.52082
H	4.47599	-1.86516	-0.91674	H	-4.45040	0.30637	2.15289
H	4.40541	-1.87832	0.86166	H	-4.40140	-1.40193	1.66217
H	7.69654	-0.02735	-2.21962	H	-7.64189	2.13551	0.70831
H	7.60606	-1.77835	-1.78525	H	-7.55223	1.25635	2.28180
H	9.11726	-0.85833	-1.49474	H	-9.07032	1.23303	1.32667
O	7.91852	-1.44937	1.02895	O	-7.92399	-1.36451	1.22266
O	7.94921	1.02005	0.37938	O	-7.92641	-0.08582	-0.98571

Table S7. Atomic coordinates (Å) and total energies (a.u.) of **ZMSM-15TPA** optimized in the S_0 and S_1 states.

S_0				S_1			
DFT/ωPBEh energy: -1543.527022286				TDDFT/ωPBEh energy: -1543.395950146			
C	7.07617	-1.96753	-0.91673	C	-6.79934	-1.33475	2.15311
S	6.29039	-0.48843	-0.22458	S	-6.24835	-0.36699	0.72027
H	8.03452	-1.62276	-1.31899	H	-7.67721	-0.80960	2.54427
H	6.48892	-2.39193	-1.73749	H	-6.03335	-1.36428	2.93598
H	7.27547	-2.73087	-0.15828	H	-7.09859	-2.35244	1.88221
C	4.73734	-1.08582	0.36754	C	-4.78027	-1.21052	0.21423
C	4.63628	-2.52882	0.77377	C	-4.76730	-2.71075	0.29413
H	4.79818	-3.20692	-0.07432	H	-4.85926	-3.07310	1.32785
H	3.64091	-2.73773	1.18154	H	-3.82767	-3.10514	-0.11150
H	5.38068	-2.77945	1.54184	H	-5.59731	-3.15179	-0.27806
C	3.68303	-0.25167	0.52620	C	-3.73950	-0.52748	-0.34025
C	4.52394	2.19390	0.12081	C	-4.52102	1.89331	-0.88970
H	2.77858	-0.68968	0.94884	H	-2.90605	-1.14195	-0.68529
C	3.60058	1.16291	0.22672	C	-3.60532	0.87912	-0.59660
N	2.40338	1.81579	0.06868	N	-2.38282	1.50180	-0.83021
N	2.59222	3.13943	-0.11355	N	-2.58080	2.78583	-1.27440
N	3.87004	3.36347	-0.07939	N	-3.87167	2.99477	-1.30203
C	1.08403	1.29442	0.06451	C	-1.08731	1.06219	-0.62386
C	0.76353	0.16971	-0.69761	C	-0.77239	0.05223	0.31747
C	0.09132	1.94320	0.80105	C	-0.02271	1.72191	-1.31653
C	-0.54078	-0.31184	-0.71144	C	0.53402	-0.34850	0.51491
C	-1.21118	1.46087	0.78586	C	1.27956	1.31930	-1.11855
C	-1.54667	0.32540	0.03090	C	1.57672	0.27170	-0.22352
H	0.35063	2.82262	1.38526	H	-0.26354	2.53361	-1.99479
H	1.52770	-0.31017	-1.30523	H	-1.56138	-0.38298	0.92448
H	-0.78985	-1.17954	-1.31798	H	0.77006	-1.09918	1.26721
N	-2.87076	-0.15615	0.01175	N	2.93063	-0.12673	-0.00337
H	-1.98037	1.96409	1.36731	H	2.08714	1.80628	-1.66407
C	-3.12438	-1.54892	-0.02174	C	3.29023	-1.45102	-0.23380
C	-3.95550	0.75649	-0.02202	C	3.84596	0.83208	0.44062
C	-5.09393	0.53157	0.76376	C	5.19311	0.80241	0.01788
C	-3.90440	1.88973	-0.84487	C	3.39467	1.89013	1.25760
C	-4.96947	2.78707	-0.86814	C	4.28926	2.86271	1.67977
C	-6.16224	1.42460	0.72044	C	6.06976	1.79216	0.43869
C	-6.10534	2.55921	-0.09019	C	5.62816	2.81999	1.27794
H	-3.02559	2.06515	-1.46238	H	2.35046	1.92016	1.55650
H	-5.13583	-0.34765	1.40388	H	5.52402	0.02780	-0.66970
H	-7.04012	1.23679	1.33658	H	7.10152	1.77491	0.09345
H	-4.91400	3.66453	-1.51038	H	3.93848	3.66559	2.32455
H	-6.93828	3.25911	-0.11543	H	6.32006	3.59461	1.60163
C	-2.38758	-2.42371	0.78971	C	2.54551	-2.21704	-1.15997
C	-4.11848	-2.07050	-0.86136	C	4.33599	-2.06637	0.49292
C	-4.36993	-3.44044	-0.88276	C	4.64812	-3.39647	0.26215
C	-2.63347	-3.79387	0.74850	C	2.88207	-3.54404	-1.38537
C	-3.62715	-4.31109	-0.08411	C	3.93212	-4.14140	-0.68344
H	-1.62370	-2.02108	1.45197	H	1.73123	-1.74462	-1.70183
H	-2.05366	-4.46015	1.38540	H	2.31693	-4.11960	-2.11541
H	-4.69211	-1.39549	-1.49313	H	4.86470	-1.50304	1.25773
H	-3.82228	-5.38145	-0.10839	H	4.18217	-5.18572	-0.85750
H	-5.14527	-3.83023	-1.54038	H	5.44468	-3.86562	0.83606
H	5.60083	2.16083	0.20784	H	-5.60150	1.85283	-0.86691

Table S8. Atomic coordinates (Å) and total energies (a.u.) of **ZMSO$_2$M-15TPA** optimized in the S_0 and S_1 states.

S_0				S_1			
DFT/ωPBEh energy: -1693.773861256				TDDFT/ωPBEh energy: -1693.653860492			
C	-5.24932	-0.27115	1.92858	C	-5.27005	0.46811	2.05137
S	-5.73989	-0.81100	0.29199	S	-5.83671	-0.58980	0.71152
H	-6.18522	-0.11408	2.47502	H	-6.16919	0.92315	2.47929
H	-4.68643	0.66358	1.86734	H	-4.60786	1.24340	1.65618
H	-4.66597	-1.06604	2.40097	H	-4.76146	-0.14949	2.79652
C	-4.19433	-1.11505	-0.59312	C	-4.38467	-1.27813	0.00036
C	-4.08649	-2.50461	-1.14569	C	-4.36425	-2.78055	-0.04373
H	-4.18568	-3.26074	-0.35839	H	-4.55689	-3.23007	0.93863
H	-3.12236	-2.63058	-1.65069	H	-3.38384	-3.11980	-0.40239
H	-4.88731	-2.70211	-1.86970	H	-5.12527	-3.18684	-0.72556
C	-3.23967	-0.18111	-0.76538	C	-3.33170	-0.52420	-0.49735
C	-4.11653	2.25027	-0.30892	C	-4.04711	1.93803	-0.92964
H	-2.34233	-0.52755	-1.28429	H	-2.48590	-1.13332	-0.81811
C	-3.18933	1.22013	-0.38832	C	-3.16396	0.87141	-0.70564
N	-1.99535	1.86235	-0.16864	N	-1.91913	1.47823	-0.92831
N	-2.18964	3.17611	0.03714	N	-2.08781	2.80901	-1.31037
N	-3.46564	3.40949	-0.05533	N	-3.36043	3.04212	-1.28760
C	-0.67806	1.33301	-0.14038	C	-0.62939	1.05099	-0.68540
C	-0.38992	0.16831	0.57273	C	-0.33567	-0.01892	0.18770
C	0.34236	2.01088	-0.81031	C	0.44197	1.75717	-1.29189
C	0.90961	-0.32403	0.60545	C	0.97555	-0.39751	0.41586
C	1.63966	1.51880	-0.77618	C	1.74848	1.37405	-1.05889
C	1.94550	0.34288	-0.06887	C	2.02717	0.28629	-0.21605
H	0.10847	2.91922	-1.35993	H	0.21039	2.59617	-1.93915
H	-1.17401	-0.33816	1.13189	H	-1.13789	-0.52155	0.71625
H	1.13142	-1.22313	1.17514	H	1.19432	-1.20419	1.11326
N	3.26180	-0.14491	-0.03092	N	3.37235	-0.12365	0.00578
H	2.42914	2.04473	-1.30766	H	2.56529	1.90289	-1.54693
C	3.51275	-1.53976	0.02524	C	3.70715	-1.46845	-0.16762
C	4.35583	0.75861	0.02351	C	4.32023	0.83467	0.38701
C	5.49268	0.53545	-0.76374	C	5.65204	0.74857	-0.06611
C	4.31593	1.87185	0.87293	C	3.92541	1.91523	1.20053
C	5.39206	2.75508	0.91963	C	4.85792	2.87466	1.57039
C	6.57215	1.41371	-0.69745	C	6.56996	1.71972	0.30887
C	6.52645	2.53005	0.13875	C	6.18103	2.78278	1.13010
H	3.43808	2.04277	1.49325	H	2.89705	1.97604	1.54695
H	5.52484	-0.33088	-1.42178	H	5.94264	-0.05872	-0.73419
H	7.45001	1.22871	-1.31426	H	7.59261	1.65892	-0.05714
H	5.34700	3.61770	1.58232	H	4.55082	3.69888	2.21021
H	7.36823	3.21830	0.18219	H	6.90524	3.54176	1.41753
C	2.82156	-2.41943	-0.81906	C	3.01362	-2.23869	-1.12533
C	4.46341	-2.05121	0.91830	C	4.69903	-2.07618	0.63161
C	4.71724	-3.42031	0.96154	C	4.99272	-3.42035	0.45973
C	3.06852	-3.78874	-0.75677	C	3.32528	-3.58136	-1.28697
C	4.01870	-4.29696	0.13051	C	4.31261	-4.17925	-0.50003
H	2.09384	-2.02183	-1.52386	H	2.25670	-1.76497	-1.74481
H	2.52551	-4.46105	-1.41907	H	2.79670	-4.16513	-2.03720
H	5.00210	-1.36924	1.57301	H	5.19998	-1.49598	1.40276
H	4.21512	-5.36652	0.17121	H	4.54708	-5.23377	-0.62652
H	5.45904	-3.80440	1.65973	H	5.74480	-3.88801	1.09158
O	-6.46445	0.28902	-0.35799	O	-6.54915	0.29440	-0.23251
O	-6.38562	-2.11975	0.44846	O	-6.58019	-1.70059	1.33506
H	-5.18744	2.20179	-0.45193	H	-5.12821	1.90823	-0.91185

Table S9. Details for the crystal structure determinations.

	ZMSM-14TPA	**4EMSM-14TPA**	**ZMSM-15TPA**
formula	$C_{24}H_{22}N_4S$	$C_{24}H_{22}N_4S$	$C_{24}H_{22}N_4S$
fw	398.5	398.5	398.5
cryst.size, mm	0.73 x 0.54 x 0.44	0.65 x 0.51 x 0.35	0.66 x 0.43 x 0.26
color, shape	yellow, block	colourless, block	colourless, block
crystal system	triclinic	monoclinic	monoclinic
space group	*P*-1 (no. 2)	*C*2/*c* (no. 15)	$P2_1/n$ (no. 14)
a, Å	8.1093(2)	20.8317(18)	8.8456(7)
b, Å	9.6000(3)	9.8784(9)	23.4528(18)
c, Å	13.0873(4)	20.8194(17)	10.1090(8)
α, °	89.2148(13)	90	90
β, °	90.597(3)	105.837(4)	104.403(2)
γ, °	86.5008(12)	90	90
V, Å^3	1012.63(5)	4121.7(6)	2031.2(3)
T, K	100	100	100
Z, Z'	2, 1	8, 1	4, 1
ρ_{calc}, g cm^{-3}	1.3070	1.2845	1.3032
μ, mm^{-1} (MoKα)	0.178	0.175	0.177
F(000)	420	1680	840
absorption corrections	multi-scan	multi-scan	multi-scan
T_{min}-T_{max}	0.89–0.93	0.90–0.94	0.91–0.96
θ range, deg	2.13–36.5	2.03–35.12	2.25–32.61
no. of rflns measd	36829	53546	25096
R_{int}	0.0286	0.0381	0.0231
no. of rflns unique	9847	9031	7412
no. of rflns $I>3\sigma(I)$	7581	6205	6390
no. of params / restraints	262 / 0	276 / 2	262 / 0
R ($I > 3\sigma(I)$) [a]	0.0419	0.0676	0.0384
R (all data)	0.0566	0.0980	0.0448
wR ($I > 3\sigma(I)$)	0.0571	0.0916	0.0536
wR (all data)	0.0580	0.0952	0.0543
GooF	2.53	2.48	2.77
Diff.Four.peaks	-0.36 / 0.51	-1.11 / 1.21	-0.36 / 0.64
CCDC no.	-	-	-

[a] $R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \Sigma w(|F_o| - |F_c|) / \Sigma w|F_o|$, GooF = $\{\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\}^{½}$