Electronic Supplementary Information for

A Leaning Amine–Ketone Dyad with a Nonconjugated Linker: Solvatofluorochromism and Dual Fluorescence Associated with Intramolecular Charge Transfer

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1. Wave Deconvolution of Fluorescence Spectra

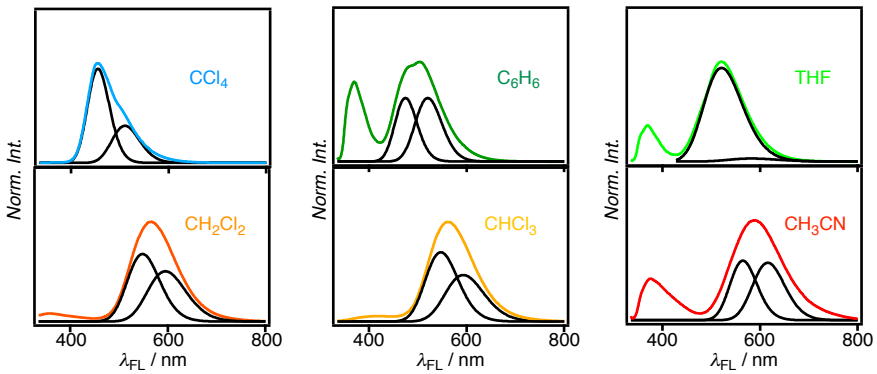

Fig. S1 Wave deconvolution of fluorescence spectra (black line) of **4** in various solvents (2.5×10^{-5} M and $\lambda_{EX} = \lambda_{AB,M} = 300$ nm).

Table S1 $\lambda_{ICT\text{-}FL,M}$ and ν_{ss} Determined by Above Fluorescence Spectra of **4** in Various Solvents

Solvents	$\lambda_{ICT\text{-}FL,M}$[a,b] / nm	ν_{ss} / 10^3 cm^{-1}
CCl_4	455, 510	19[c]
C_6H_6	475, 520	12[c]
THF	519, 586	14[c]
$CHCl_3$	547, 593	15[c]
CH_2Cl_2	548, 595	15[c]
CH_3CN	564, 615	16[c]

(a) [**4**] = 2.5×10^{-5} M. (b) $\lambda_{EX} = 300$ nm. (d) The value related to shorter $\lambda_{ICT\text{-}FL,M}$.

2. Excitation Spectra

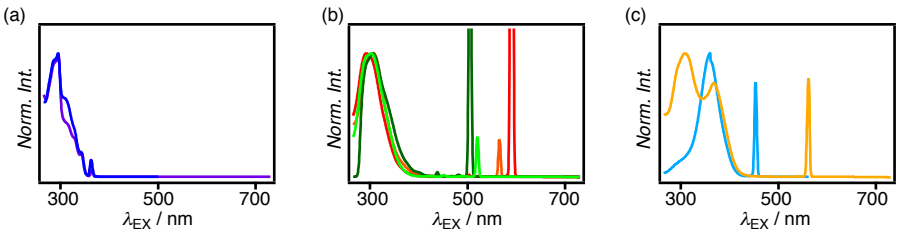

Fig. S2 Excitation spectra of **4** in (a) saturated hydrocarbons (*c*-C_6H_{12} and *n*-C_6H_{14}), (b) aprotic solvents except for CCl_4 and $CHCl_3$ (C_6H_6, THF, CH_2Cl_2, and CH_3CN), and (c) CCl_4 and $CHCl_3$ ([**4**] = 2.5×10^{-5} M and $\lambda_{DET} = \lambda_{FL,M}$).

3. Crystallographic Data of Dyad 4

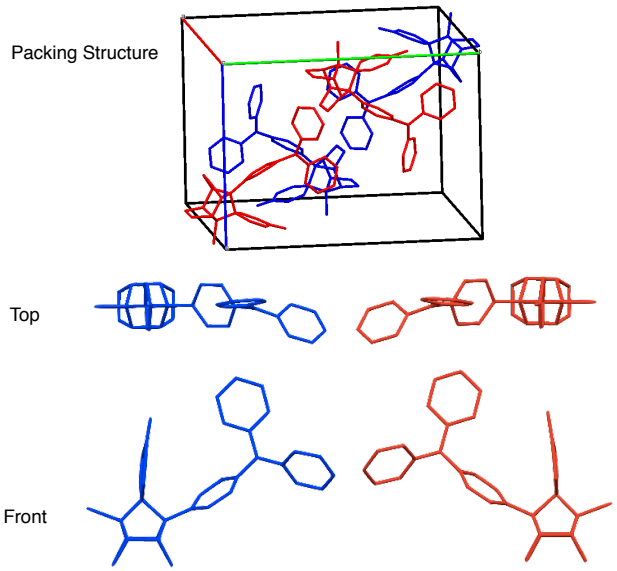

Fig. S3 Packing structure and molecular structure of **4** in the crystalline state.

4. Cyclic Voltammogram

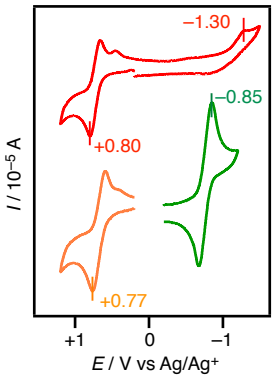

Fig. S4 Cyclic voltammograms of **4** (red), TPA-^{t}Bu, (orange) and benzoquinone (green) in CH_2Cl_2 containing 0.1 M *n*-$Bu_4N^+BF_4^-$.

Scan rate: 0.1 Vs^{-1}, reference electrode: Ag/Ag^+, working and counter electrodes: Pt.

5. NMR Spectra

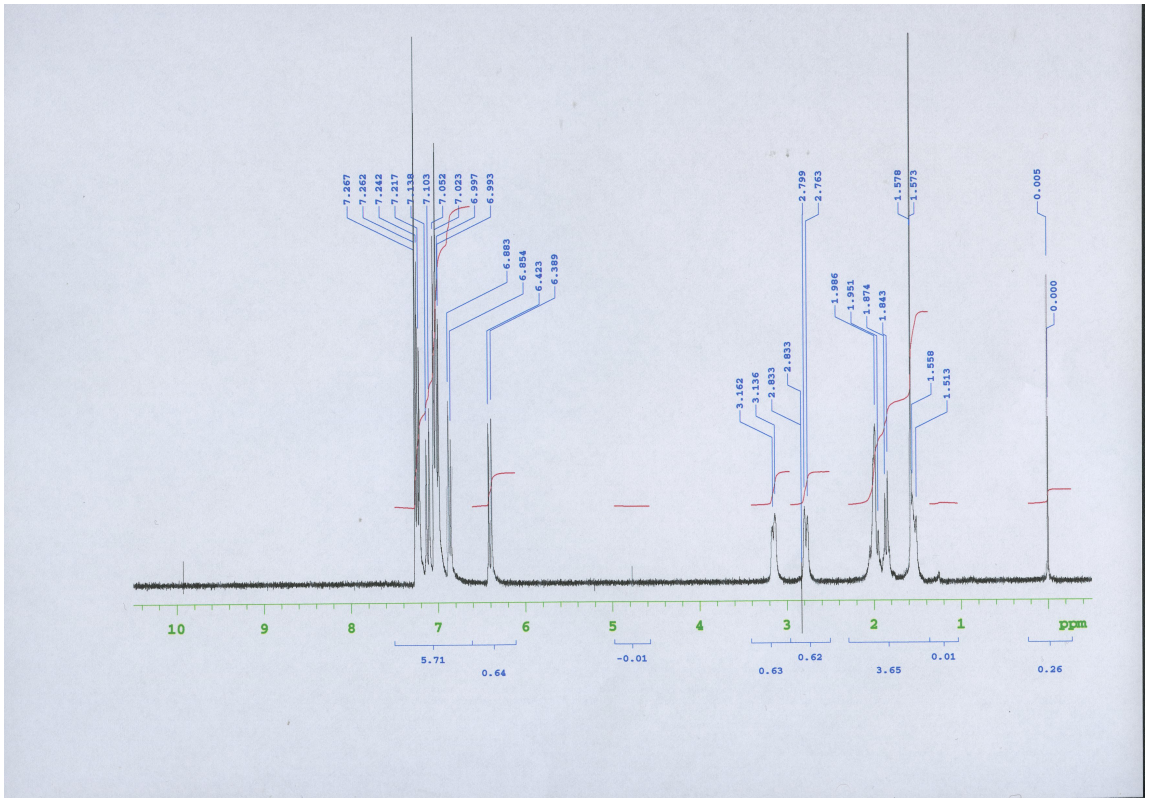

Fig. S5 ^{1}H NMR spectrum of **4** (300 MHz, $CDCl_3$).

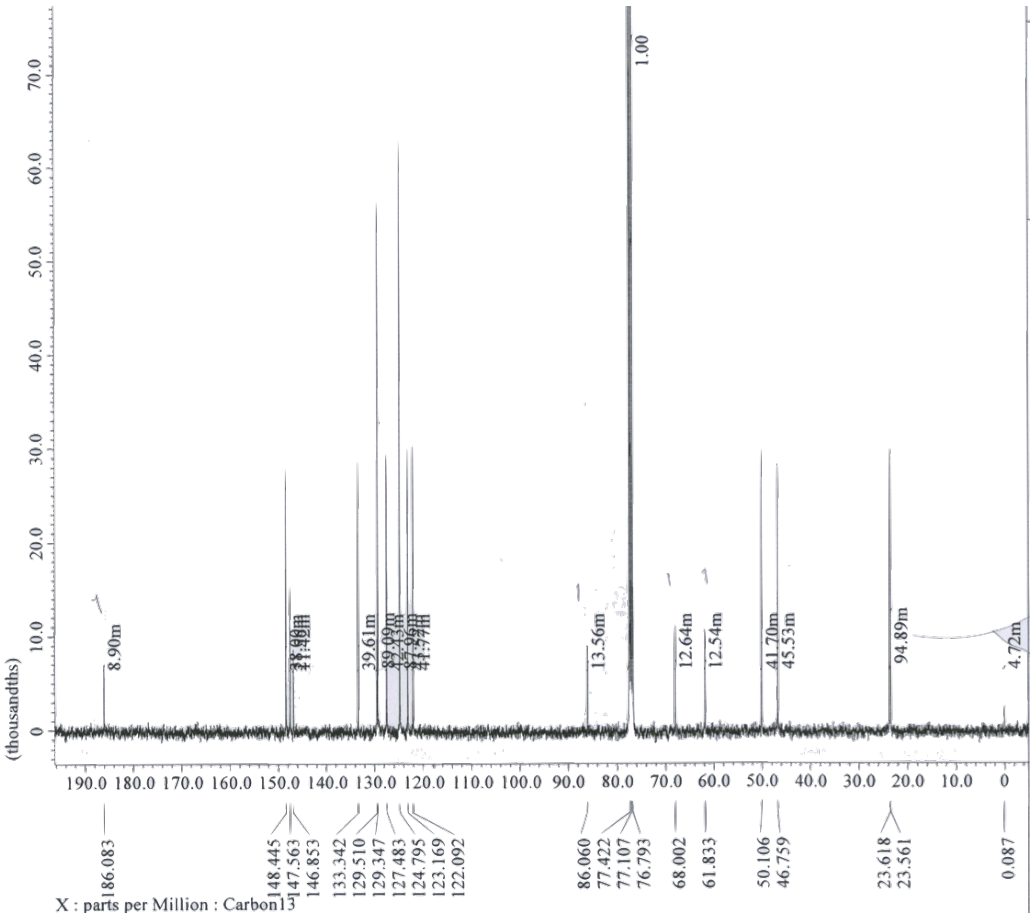

Fig. S6 ^{13}C NMR spectrum of **4** (100 MHz, in $CDCl_3$).

6. Calculated Cartesian Coordinates

Geometry optimizations for **4**, TPA-^{t}Bu, **7**, LE-**4***, and ICT-**4*** by employing DFT method were performed using Gaussian 09 with the B3LYP functional and 6-31G* basis set. No imaginary frequencies were found. Cartesian coordinates for optimized geometries of **4**, TPA-^{t}Bu, **7**, LE-**4***, and ICT-**4*** were given in Tables S2, S3, S4, S5, and S6, respectively.

Table S2 The Cartesian Coordinates of **4** Optimized at the B3LYP/6-31G* Level

Atom	Coordinates / Å		
	X	Y	Z
C	2.15538	–0.62506	–0.21439
C	2.92807	0.67362	0.29102
C	0.64070	–0.53912	–0.18735
C	2.80036	–0.95210	–1.60856
C	2.80969	–1.80769	0.58266
C	2.67492	1.87431	–0.57344
C	2.66440	0.95602	1.74185
C	4.30762	0.01454	0.02689
C	4.31504	–1.35098	0.75672
C	4.30485	–0.49248	–1.43749
Cl	5.73600	1.05880	0.43028
H	4.55681	–1.25659	1.81807
C	5.39410	–2.15877	0.00667
H	4.53884	0.29783	–2.15478
C	5.38786	–1.59112	–1.44330
H	2.37631	–1.95476	1.57428
C	2.54762	–3.03029	–0.32003
H	2.35070	–0.39224	–2.43166
C	2.53773	–2.46351	–1.76878
H	6.36490	–1.98159	0.47926
H	5.21872	–3.23680	0.04786
H	6.35561	–1.13744	–1.67723
H	5.20893	–2.35563	–2.20371
H	1.56983	–3.45515	–0.07143
H	3.27962	–3.82915	–0.17558
H	1.55234	–2.60402	–2.22474
H	3.25850	–2.95408	–2.42826
C	–0.06685	0.11554	–1.20946
C	–0.11983	–1.06092	0.87052
C	–1.50613	–0.94023	0.91206
C	–1.45256	0.23274	–1.18885
C	–2.19892	–0.29252	–0.12187
H	0.37027	–1.56275	1.69854
H	–2.05784	–1.34672	1.75348
H	0.46805	0.54287	–2.05173
H	–1.96437	0.73565	–2.00286
N	–3.60987	–0.16754	–0.09043
C	–4.41572	–1.24044	0.38040
C	–4.22623	1.03961	–0.52869
C	–3.70452	2.28531	–0.14575
C	–5.36559	0.99889	–1.34756
C	–5.97254	2.18204	–1.76502
C	–4.30724	3.46324	–0.58379
C	–5.44616	3.42028	–1.39088
H	–5.77000	0.03836	–1.65115
H	–6.85463	2.13319	–2.39825
H	–2.82836	2.32445	0.49380
H	–3.89014	4.41901	–0.27790
H	–5.91788	4.34046	–1.72368
C	–5.51998	–0.99027	1.21105
C	–4.12537	–2.56535	0.01599
C	–4.91681	–3.61301	0.48286
C	–6.31639	–2.04301	1.65767
C	–6.01902	–3.36039	1.30229
H	–3.27999	–2.76607	–0.63451
H	–4.67746	–4.63203	0.18980
H	–5.74809	0.03039	1.50101
H	–7.16717	–1.83051	2.29985
H	–6.63826	–4.17877	1.65829
H	2.87397	0.15550	2.44590
C	2.17306	2.11562	2.20374
H	2.89933	1.77612	–1.63216
C	2.18825	3.03836	–0.11773
H	1.97926	2.27328	3.26116
H	2.00924	3.88128	–0.77957
C	1.87132	3.25141	1.30923
O	1.39721	4.30542	1.72435

Table S3 The Cartesian Coordinates of TPA-^{t}Bu Optimized at the B3LYP/6-31G* Level

Atom	Coordinates / Å		
	X	Y	Z
C	–0.00323	–0.01689	–0.06425
N	1.20715	0.13631	0.66443
C	–1.01422	0.95513	0.01423
C	–0.20951	–1.14635	–0.87352
C	–1.40226	–1.29982	–1.57743
C	–2.19616	0.80125	–0.70783
C	–2.40173	–0.32717	–1.50443
H	0.56892	–1.89931	–0.94460
H	–1.54313	–2.18075	–2.19851
H	–0.86709	1.82772	0.64262
H	–2.96704	1.56406	–0.63386
H	–3.32737	–0.44696	–2.06017
C	1.83334	1.40839	0.75332
C	1.78546	–0.98615	1.31947
C	0.99268	–1.88827	2.03892
C	3.16811	–1.22134	1.25940
C	3.72606	–2.31822	1.90706
C	1.56501	–2.99407	2.66802
C	2.94417	–3.23961	2.62603
H	3.80268	–0.53877	0.70252
H	4.80098	–2.46219	1.83395
H	–0.07858	–1.72455	2.10421
H	0.90745	–3.66366	3.21176
C	3.60557	–4.44576	3.31540
C	2.40254	1.84102	1.96250
C	1.89666	2.25394	–0.36682
C	2.50635	3.50328	–0.27215
C	3.02614	3.08475	2.04192
C	3.07912	3.92670	0.92916
H	1.46618	1.92550	–1.30743
H	2.54538	4.14317	–1.15001
H	2.35224	1.19743	2.83494
H	3.46046	3.40179	2.98664

H	3.55968	4.89852	0.99704
C	4.31510	–5.32068	2.25430
C	4.64735	–3.94683	4.34478
C	2.58375	–5.32746	4.05801
H	3.59859	–5.69929	1.51633
H	5.08569	–4.76062	1.71409
H	4.80077	–6.18187	2.72979
H	5.42985	–3.34351	3.87275
H	4.17090	–3.33147	5.11652
H	5.13428	–4.79642	4.83934
H	2.06440	–4.77278	4.84790
H	1.83026	–5.74046	3.37769
H	3.09881	–6.17110	4.53111

Table S4 The Cartesian Coordinates of **7** Optimized at the B3LYP/6-31G* Level

Atom	Coordinates / Å		
	X	Y	Z
C	2.11355	–0.61884	–0.25103
C	2.87662	0.57226	0.45142
C	2.80301	–0.77611	–1.64626
C	2.68703	–1.91498	0.41072
C	2.67944	1.87967	–0.26171
C	2.55659	0.67433	1.91562
C	4.25566	–0.08192	0.16704
C	4.19501	–1.53276	0.71132
C	4.31134	–0.39060	–1.35167
Cl	5.68477	0.85889	0.76849
H	4.38893	–1.58479	1.78536
C	5.29066	–2.26449	–0.09151
H	4.59931	0.48052	–1.94504
C	5.36739	–1.51085	–1.45282
H	2.18078	–2.16802	1.34760
C	2.44472	–3.00028	–0.65946
H	2.39198	–0.09444	–2.39755
C	2.52145	–2.24662	–2.02067
H	6.24149	–2.17842	0.44281
H	5.09052	–3.33326	–0.20231
H	6.35552	–1.05868	–1.57988
H	5.20956	–2.16352	–2.31521
H	1.44995	–3.43546	–0.51554
H	3.15199	–3.83081	–0.59110
H	1.56463	–2.30897	–2.55007
H	3.27074	–2.66429	–2.69803
H	2.71624	–0.21554	2.51852
C	2.07975	1.78124	2.50553
H	2.93273	1.90832	–1.31806
C	2.20295	2.98999	0.32202
H	1.84984	1.80937	3.56717
H	2.06430	3.91344	–0.23364
C	1.84736	3.03254	1.75531
O	1.39424	4.04153	2.28831
C	0.59496	–0.49888	–0.27023
H	0.19190	–0.44777	0.74734
H	0.27903	0.40788	–0.79798
H	0.12947	–1.35490	–0.77046

Table S5 The Cartesian Coordinates of LE-**4*** Optimized at the TD-B3LYP/6-31G* Level

Atom	Coordinates / Å		
	X	Y	Z
C	2.11279	–0.69861	–0.10835
C	2.86737	0.68033	0.17403
C	0.60532	–0.60562	–0.10083
C	2.73197	–1.25333	–1.43736
C	2.75721	–1.74610	0.85856
C	2.62293	1.75396	–0.86274
C	2.61198	1.22559	1.56236
C	4.24676	–0.03569	0.01207
C	4.26259	–1.26031	0.95310
C	4.23958	–0.77692	–1.34697
Cl	5.69465	1.03386	0.22311
H	4.49707	–0.98744	1.98417
C	5.33855	–2.18316	0.34642
H	4.46675	–0.11269	–2.18335
C	5.31415	–1.87284	–1.18110
H	2.33519	–1.73032	1.86671
C	2.50464	–3.10266	0.16404
H	2.27935	–0.82417	–2.33519
C	2.46810	–2.77098	–1.35704
H	6.31123	–1.91442	0.76959
H	5.18104	–3.24151	0.57410
H	6.28104	–1.47169	–1.49989
H	5.12593	–2.75790	–1.79605
H	1.53932	–3.50886	0.48990
H	3.25277	–3.85856	0.41718
H	1.47484	–2.98470	–1.77083
H	3.17643	–3.36430	–1.94202
C	–0.07276	0.02696	–1.16291
C	–0.17764	–1.08999	0.96315
C	–1.56255	–0.96656	0.97466
C	–1.45394	0.17154	–1.16586
C	–2.20404	–0.33004	–0.09438
H	0.30278	–1.55897	1.81254
H	–2.13975	–1.32653	1.82077
H	0.49661	0.43541	–1.98634
H	–1.95247	0.65933	–1.99772
N	–3.63188	–0.16273	–0.07821
C	–4.45243	–1.26572	0.20584
C	–4.16597	1.11122	–0.32060
C	–3.44402	2.26096	0.07789
C	–5.40576	1.25408	–0.98726
C	–5.91002	2.52213	–1.23444
C	–3.96746	3.52012	–0.17371
C	–5.19843	3.65815	–0.82765
H	–5.93188	0.37400	–1.33937
H	–6.85094	2.62962	–1.76468
H	–2.49924	2.15387	0.59655
H	–3.41458	4.39689	0.14552
H	–5.59753	4.64738	–1.02739
C	–5.64237	–1.10257	0.94953
C	–4.07090	–2.55268	–0.23232
C	–4.87903	–3.64372	0.05371
C	–6.43518	–2.20668	1.23195
C	–6.06205	–3.47872	0.78414

H	–3.16308	–2.67154	–0.81164
H	–4.59099	–4.62828	–0.30035
H	–5.90754	–0.12270	1.32988
H	–7.33841	–2.07900	1.82004
H	–6.68546	–4.33811	1.00929
H	2.79915	0.55932	2.40177
C	2.19649	2.50018	1.80850
H	2.85042	1.50970	–1.89859
C	2.21399	3.02208	–0.55656
H	2.04616	2.82212	2.83841
H	2.08865	3.74887	–1.35856
C	1.95445	3.50378	0.78549
O	1.56440	4.68745	1.04475

Table S6 The Cartesian Coordinates of ICT-**4*** Optimized at the TD-B3LYP/6-31G* Level

Atom	Coordinates / Å		
	X	Y	Z
C	–2.19698	–0.80525	0.13741
C	–2.68302	0.69115	–0.17973
C	–0.69335	–0.91889	0.21592
C	–3.00212	–1.24780	1.40272
C	–2.93390	–1.71349	–0.89836
C	–2.31638	1.69289	0.89105
C	–2.22289	1.18662	–1.53189
C	–4.16534	0.22807	–0.13099
C	–4.32320	–0.97457	–1.09078
C	–4.39118	–0.50929	1.21193
Cl	–5.38767	1.53663	–0.43286
H	–4.43443	–0.66395	–2.13196
C	–5.58356	–1.70060	–0.57798
H	–4.56067	0.17921	2.04262
C	–5.62827	–1.39306	0.94903
H	–2.43923	–1.76107	–1.87130
C	–2.96454	–3.09719	–0.21601
H	–2.55588	–0.91223	2.34207
C	–3.00649	–2.78846	1.30977
H	–6.46281	–1.27874	–1.07439
H	–5.58362	–2.77131	–0.80165
H	–6.52968	–0.82259	1.19277
H	–5.65230	–2.29439	1.56829
H	–2.04841	–3.64504	–0.46785
H	–3.79623	–3.72400	–0.54951
H	–2.10849	–3.18021	1.80249
H	–3.85945	–3.24846	1.81654
C	–0.00886	–0.47636	1.36239
C	0.08374	–1.31919	–0.88551
C	1.47103	–1.19954	–0.88716
C	1.37373	–0.33143	1.37371
C	2.10796	–0.66274	0.23320
H	–0.40069	–1.67929	–1.78458
H	2.04440	–1.44749	–1.77537
H	–0.56817	–0.17149	2.23674
H	1.87709	0.07742	2.24457
N	3.50548	–0.29575	0.16073
C	4.46841	–1.27532	–0.11252
C	3.80305	1.06577	0.29421
C	2.81888	2.02992	–0.04759
C	5.05012	1.49361	0.81900
C	5.29158	2.84830	0.97936
C	3.07327	3.38049	0.12400
C	4.31227	3.79412	0.63331
H	5.78297	0.76202	1.14006
H	6.23722	3.17481	1.40114
H	1.86496	1.73023	–0.45842
H	2.27848	4.07399	–0.13591
H	4.51465	4.85148	0.77336
C	5.61080	–0.97605	–0.88787
C	4.27203	–2.59016	0.36308
C	5.21706	–3.56926	0.09265
C	6.54323	–1.97021	–1.15350
C	6.35672	–3.26655	–0.66228
H	3.39296	–2.81490	0.95563
H	5.06905	–4.57403	0.47550
H	5.73139	0.01676	–1.30578
H	7.41027	–1.73838	–1.76409
H	7.08846	–4.03921	–0.87592
H	–2.59039	0.66397	–2.41167
C	–1.36508	2.23568	–1.69079
H	–2.76813	1.57007	1.87268
C	–1.45872	2.73475	0.67882
H	–1.04697	2.52084	–2.69276
H	–1.21760	3.40565	1.50257
C	–0.86095	3.05063	–0.60215
O	0.01111	3.97605	–0.76639

7. Results of TD-DFT Calculations

Table S7. Major Electronic Transitions of **4** and its Component (HOMO: 133, LUMO: 134)

Wavelength / nm	*f*	Orbitals	CI Coefficient
423	0.0180	133 → 134	0.70550
319	0.0155	133 → 135	0.55186
		133 → 136	–0.41964
310	0.4124	133 → 135	0.42419
		133 → 136	0.55512
300	0.2101	133 → 137	0.69200
237	0.1032	123 → 134	-0.13073
		126 → 134	0.44207
		129 → 134	0.12791
		132 → 135	-0.28426
		132 → 136	0.16892
		132 → 138	-0.27953
		132 → 140	0.15375
		133 → 141	0.12206
		133 → 142	-0.10115

Table S8. Major Electronic Transitions of TPA-^{t}Bu and its Component (HOMO: 81, LUMO: 82)

Wavelength / nm	*f*	Orbitals	CI Coefficient
318	0.0161	81 → 82	0.68692
		81 → 84	–0.11761
303	0.3114	81 → 83	–0.43108
		81 → 84	0.54300
302	0.2674	81 → 83	0.54733
		81 → 84	0.42186

Table S9. Major Electronic Transitions of **7** and its Component (HOMO: 73, LUMO: 74)

Wavelength / nm	*f*	Orbitals	CI Coefficient
379	0.0000	73 → 74	0.70327
247	0.0111	71 → 74	0.69864
241	0.2791	69 → 74	–0.22192
		71 → 75	0.17381
		71 → 74	0.64326

(EOF)