Electronic Supporting Information

meta-Terphenyl Linked Donor–π–Acceptor Dyads: Intramolecular Charge Transfer Controlled by Electron Acceptor Group Tuning

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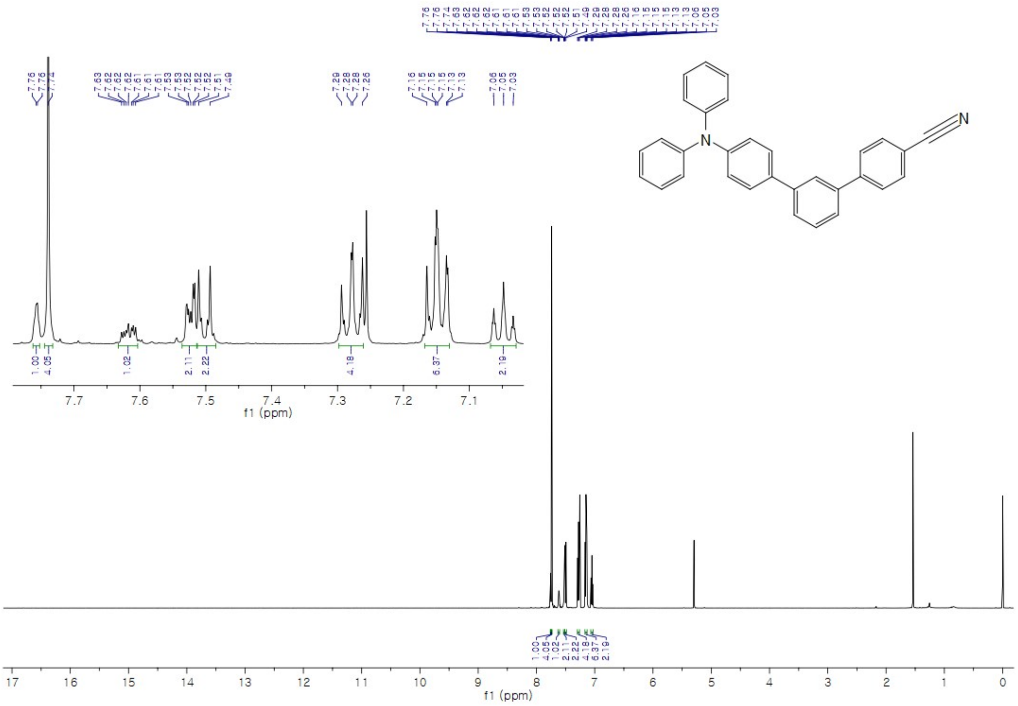


Figure S1. ^{1}H-NMR spectrum of **Cya** in $CDCl_3$ (500MHz, 293K)

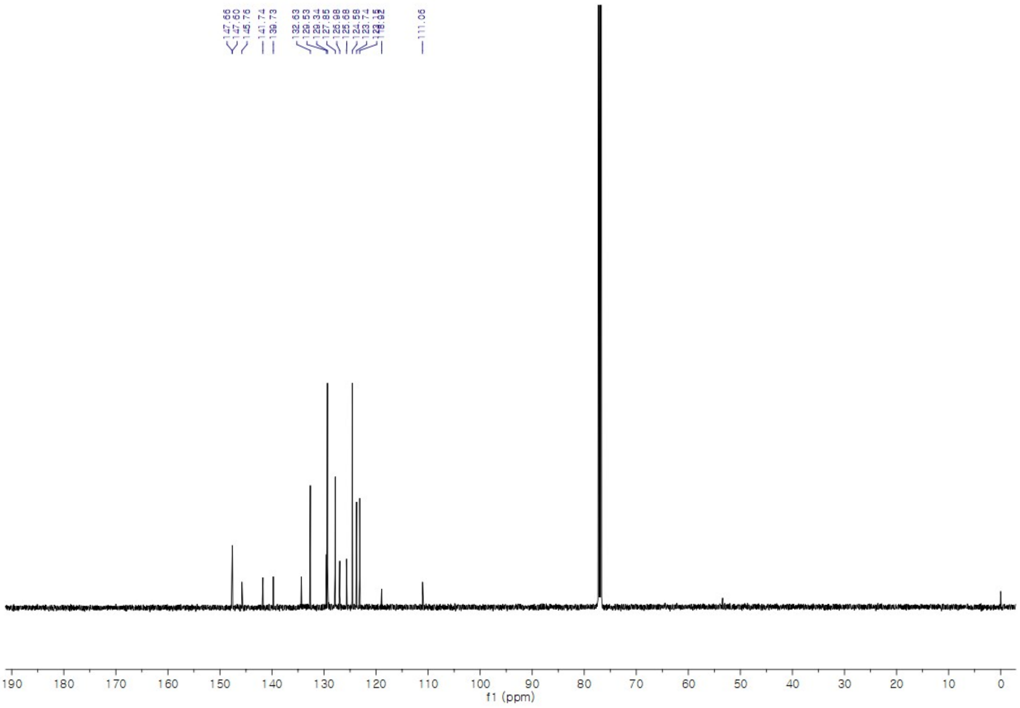


Figure S2. $^{13}C\{^1H\}$-NMR spectrum of **Cya** in $CDCl_3$ (125MHz, 293K)

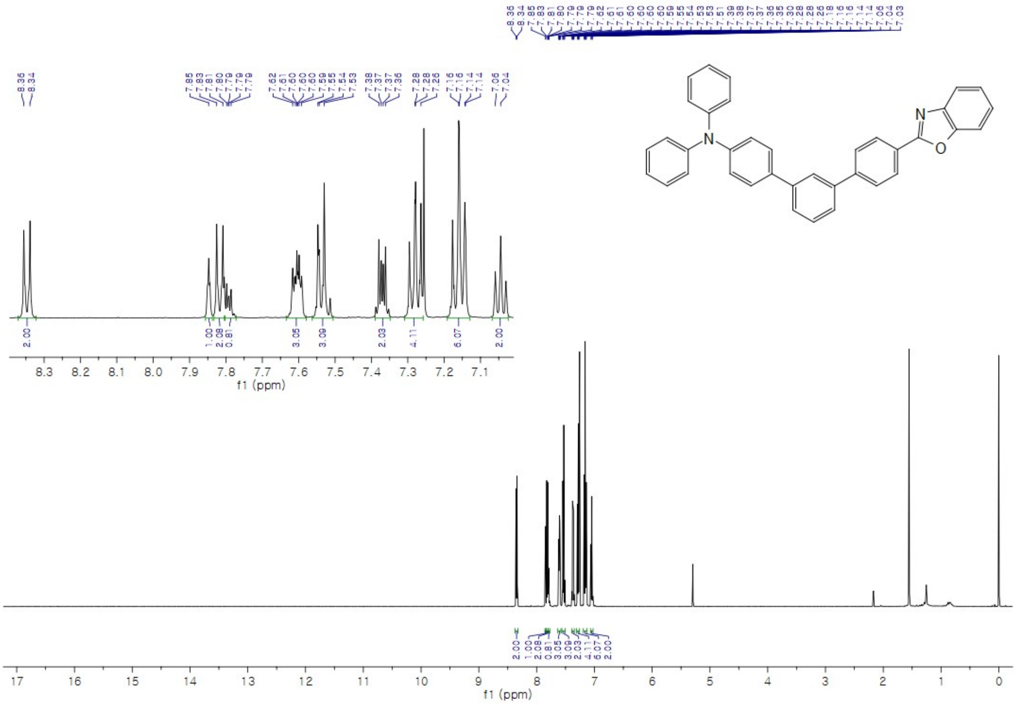


Figure S3. ^1H-NMR spectrum of **Oxa** in $CDCl_3$ (500MHz, 293K)

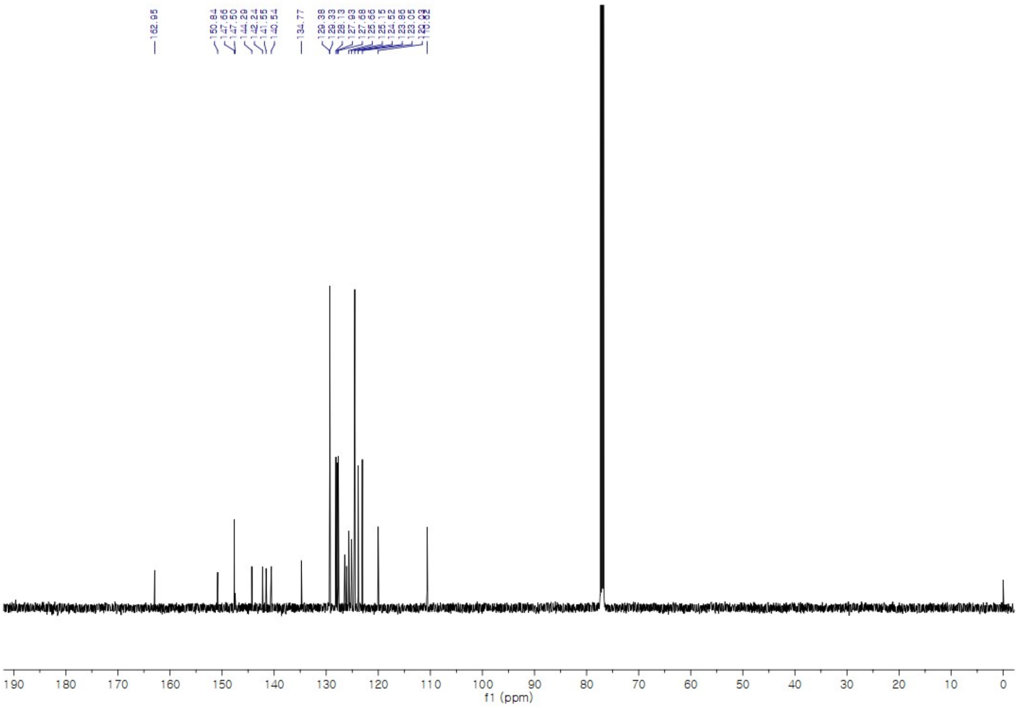


Figure S4. $^{13}C\{^1H\}$-NMR spectrum of **Oxa** in $CDCl_3$ (125MHz, 293K)

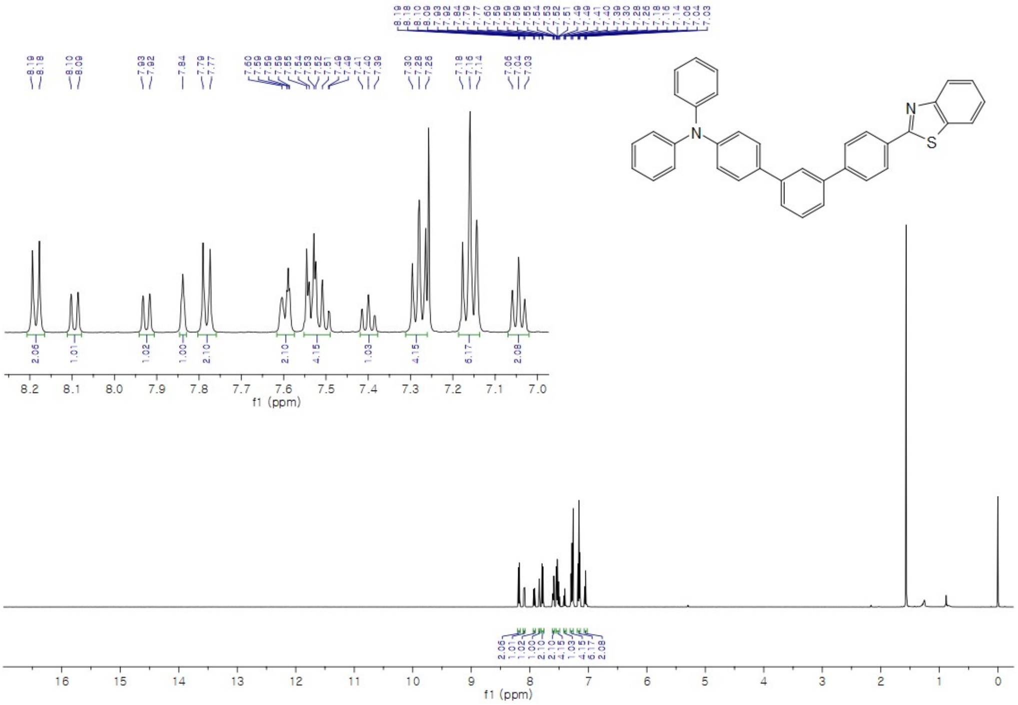


Figure S5. ^{1}H-NMR spectrum of **Thia** in $CDCl_3$ (500MHz, 293K)

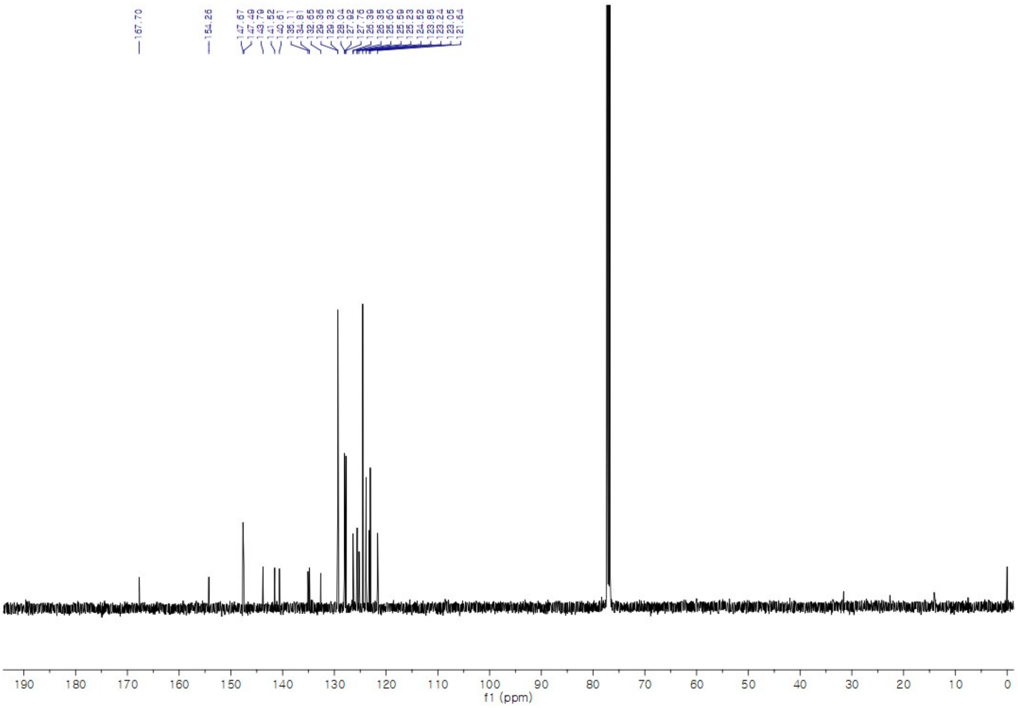


Figure S6. $^{13}C\{^{1}H\}$-NMR spectrum of **Thia** in $CDCl_3$ (125MHz, 293K)

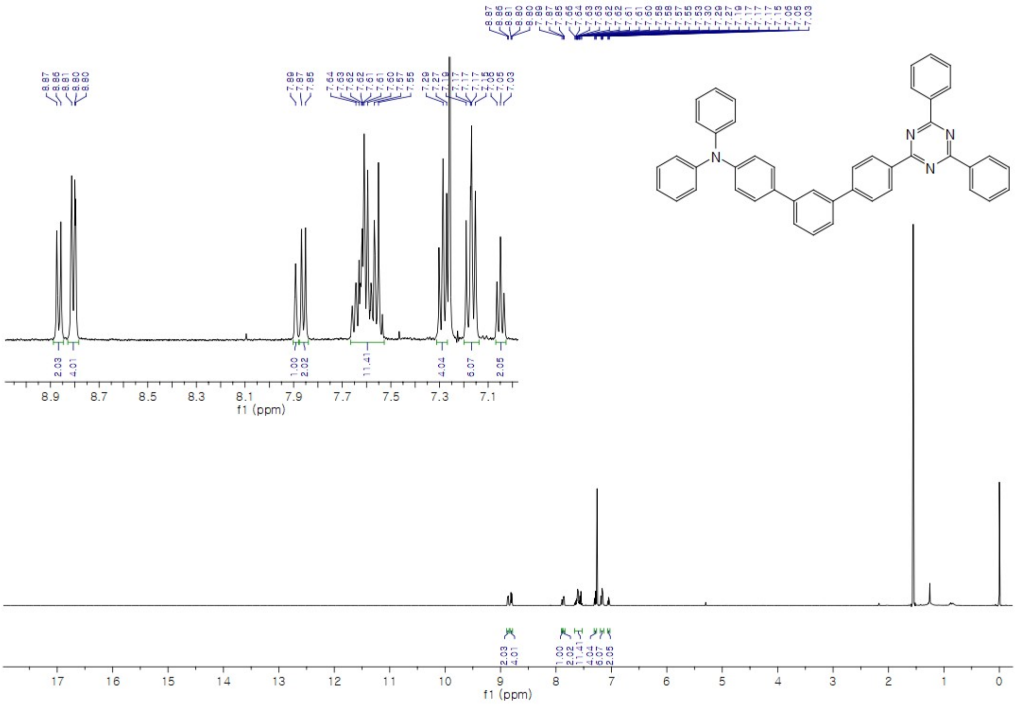


Figure S7. ^{1}H-NMR spectrum of **Tria** in $CDCl_3$ (500MHz, 293K)

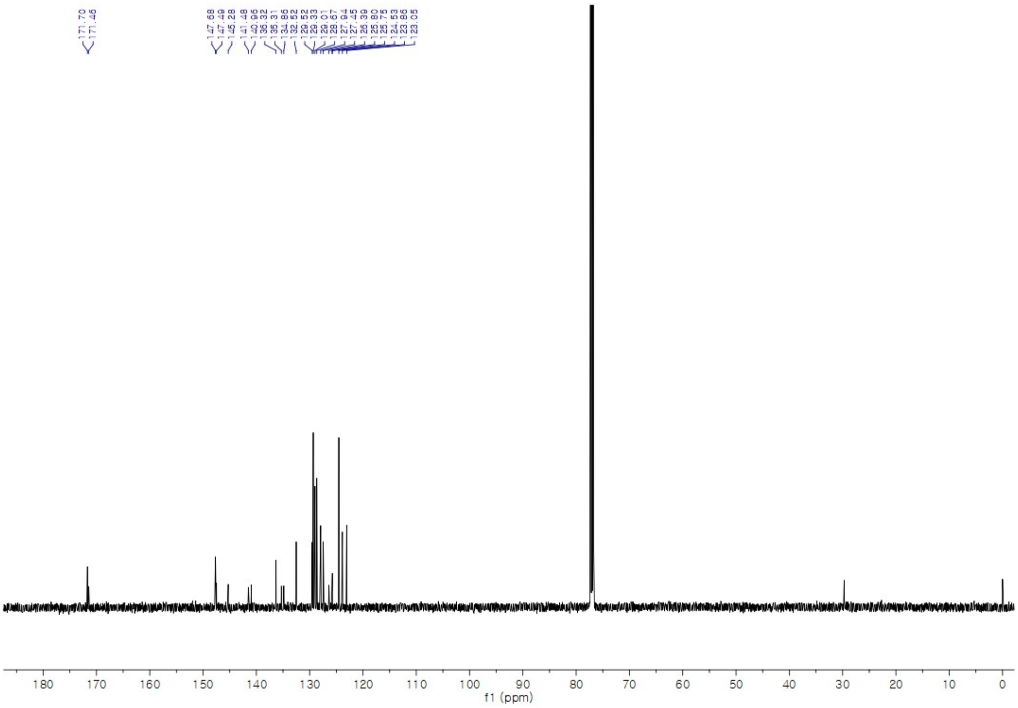
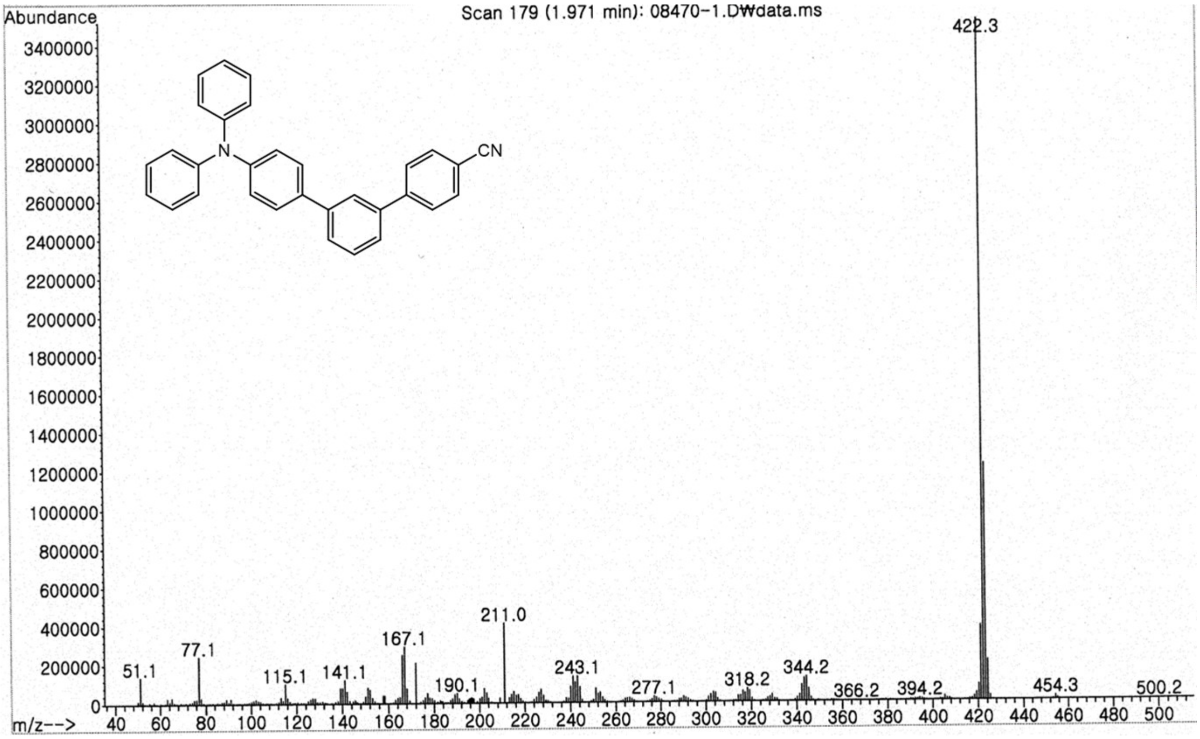


Figure S8. $^{13}C\{^{1}H\}$-NMR spectrum of **Tria** in $CDCl_3$ (125MHz, 293K)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2400000
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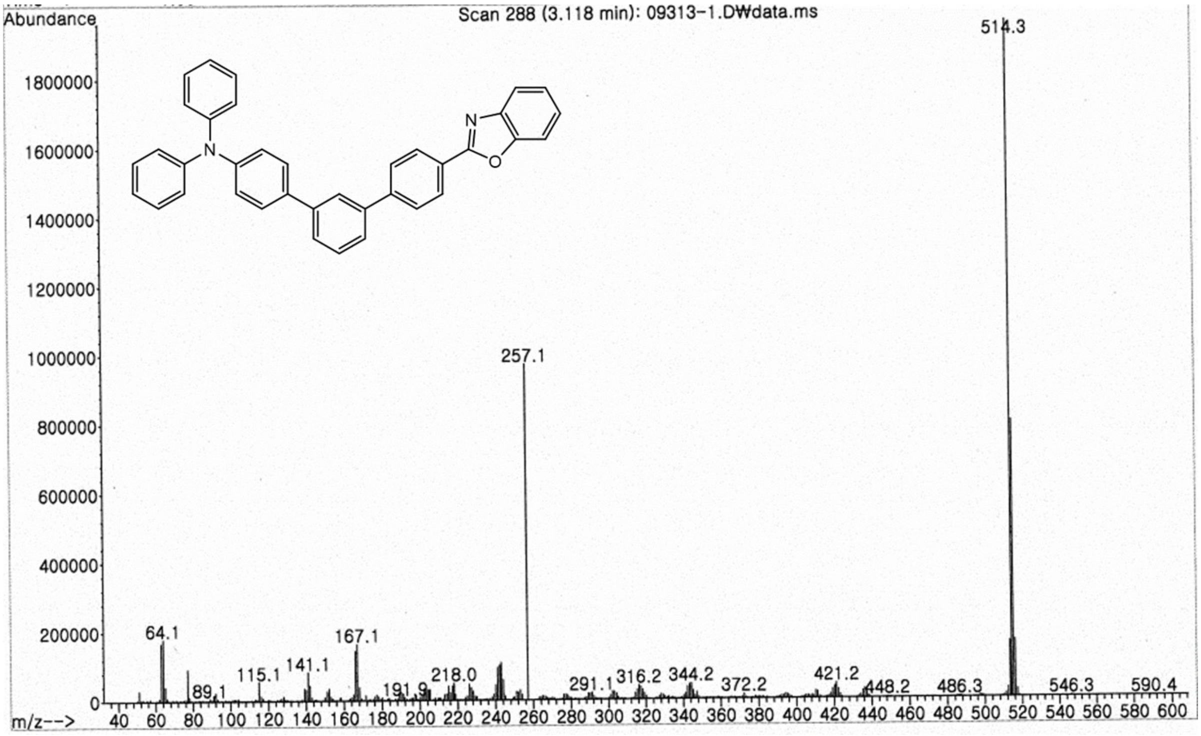
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500
N
CN
422.3
51.1
77.1
115.1
141.1
167.1
190.1
211.0
243.1
277.1
318.2
344.2
366.2
394.2
454.3
500.2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N
N
O
514.3
257.1
64.1
89.1
115.1
141.1
167.1
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486.3
546.3
590.4

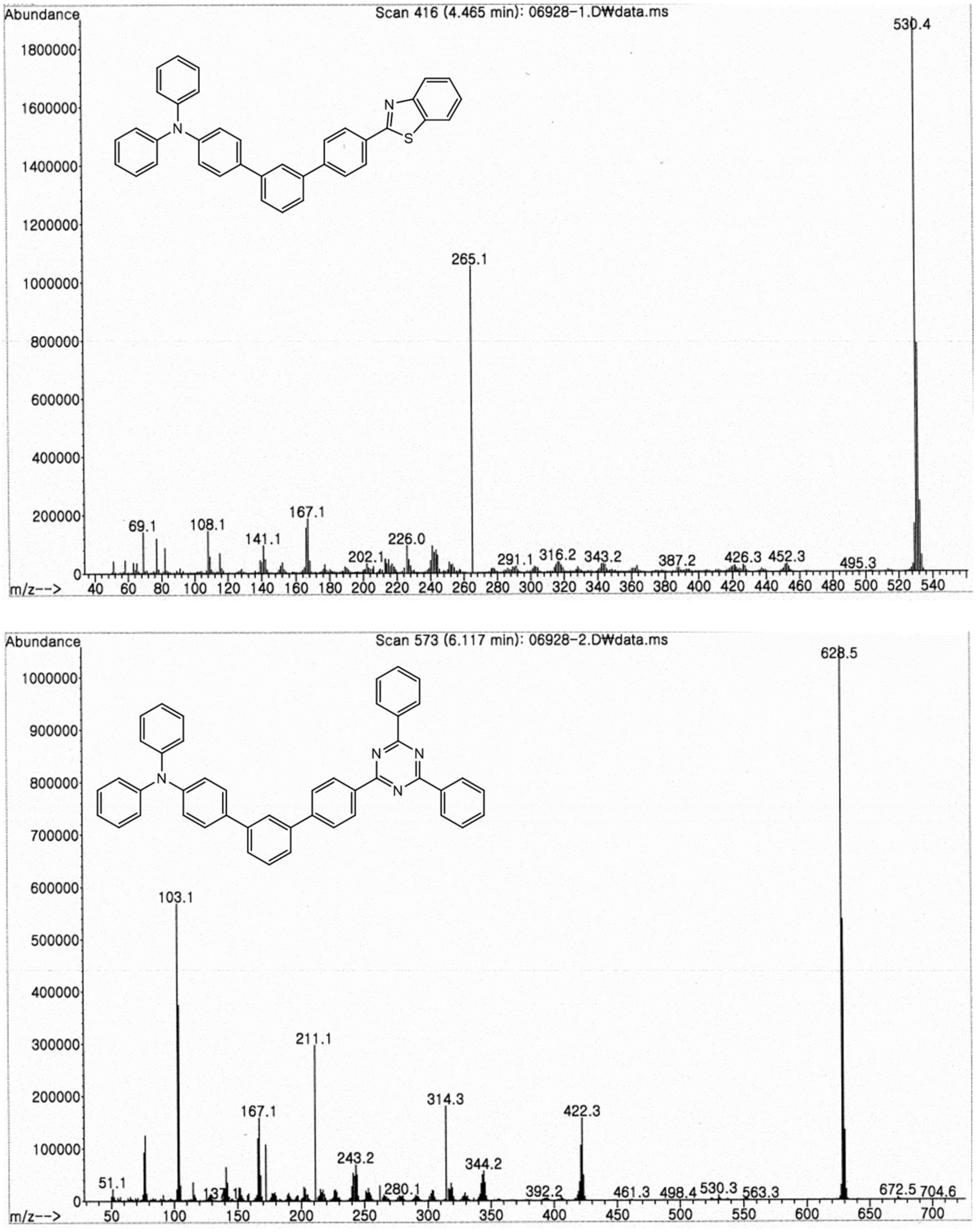

Figure S9. GC-MS data of **Cya–Tria**.

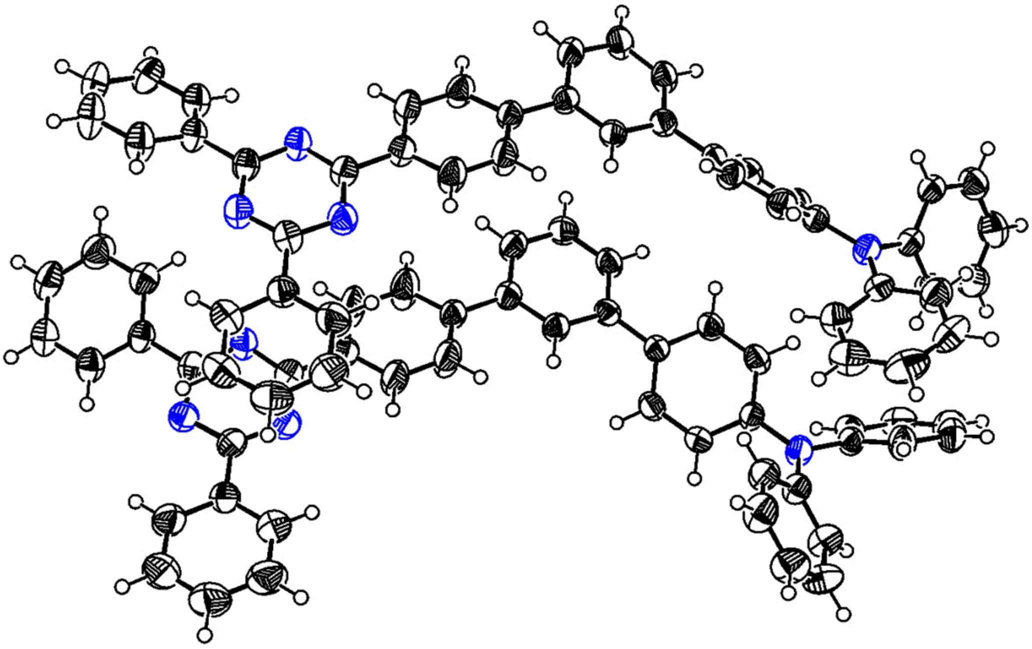

Figure S10. ORTEP drawings of **Tria**. Ellipsoid contour percent probability level is 50%. The white, gray, and blue color refer to H, C, and N atoms.

Table S1. Crystal data and structure refinement for **Tria**

Comp.	**Tria**	
Empirical formula	$C_{45} H_{32} N_4$	
Formula weight	628.74	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.945(6) Å	α = 91.599(15)°.
	b = 18.098(8) Å	β = 94.106(17)°.
	c = 18.778(10) Å	γ = 104.334(16)°.
Volume	3263(3) $Å^3$	
Z	4	
Density (calculated)	1.280 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	1320	
Crystal size	0.211 x 0.140 x 0.048 mm^3	
Theta range for data collection	2.121 to 26.000°.	
Index ranges	-12<=h<=12, -22<=k<=22, -23<=l<=23	
Reflections collected	79354	
Independent reflections	12825 [R(int) = 0.1893]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.5900	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12825 / 0 / 883	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0725, wR2 = 0.1612	
R indices (all data)	R1 = 0.2074, wR2 = 0.2514	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.266 and -0.262 e.$Å^{-3}$	

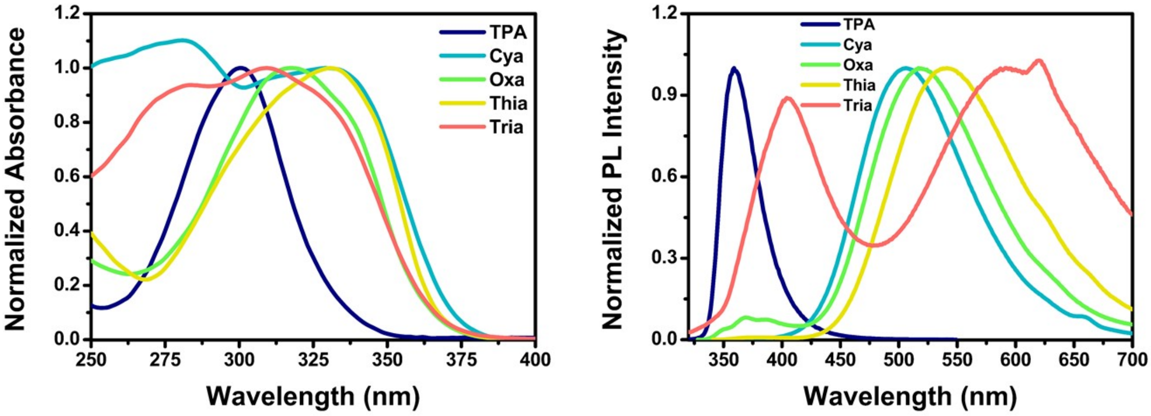

Figure S11. UV-vis absorption (left) and emission (right) spectra of triphenylamine (TPA), and all dyads in dichloromethane solution.

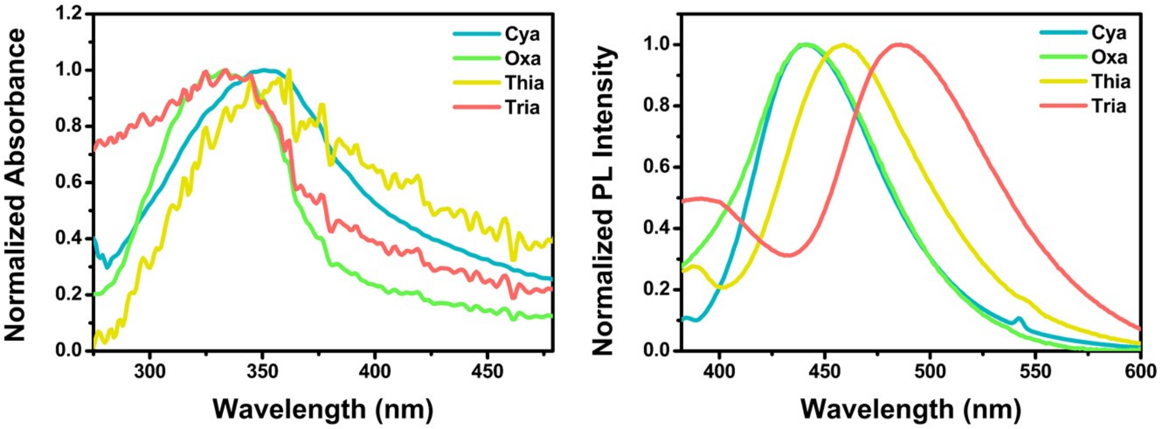

Figure S12. UV-vis absorption (left) and emission (right) spectra of **Cya**–**Tria** in the solid state.

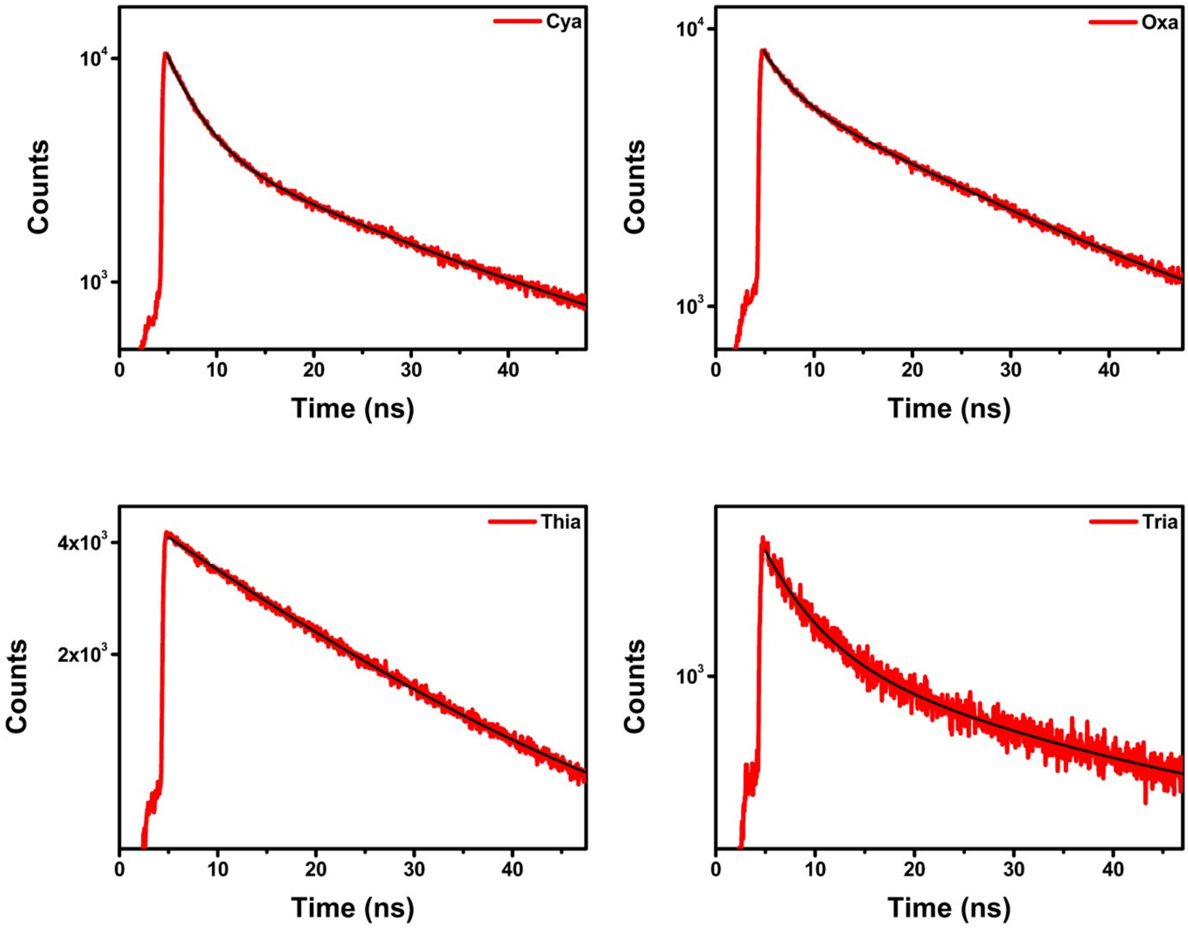

Figure S13. Fluorescence lifetimes (τ_{em}) of **Cya**–**Tria** in dichloromethane solution at RT.

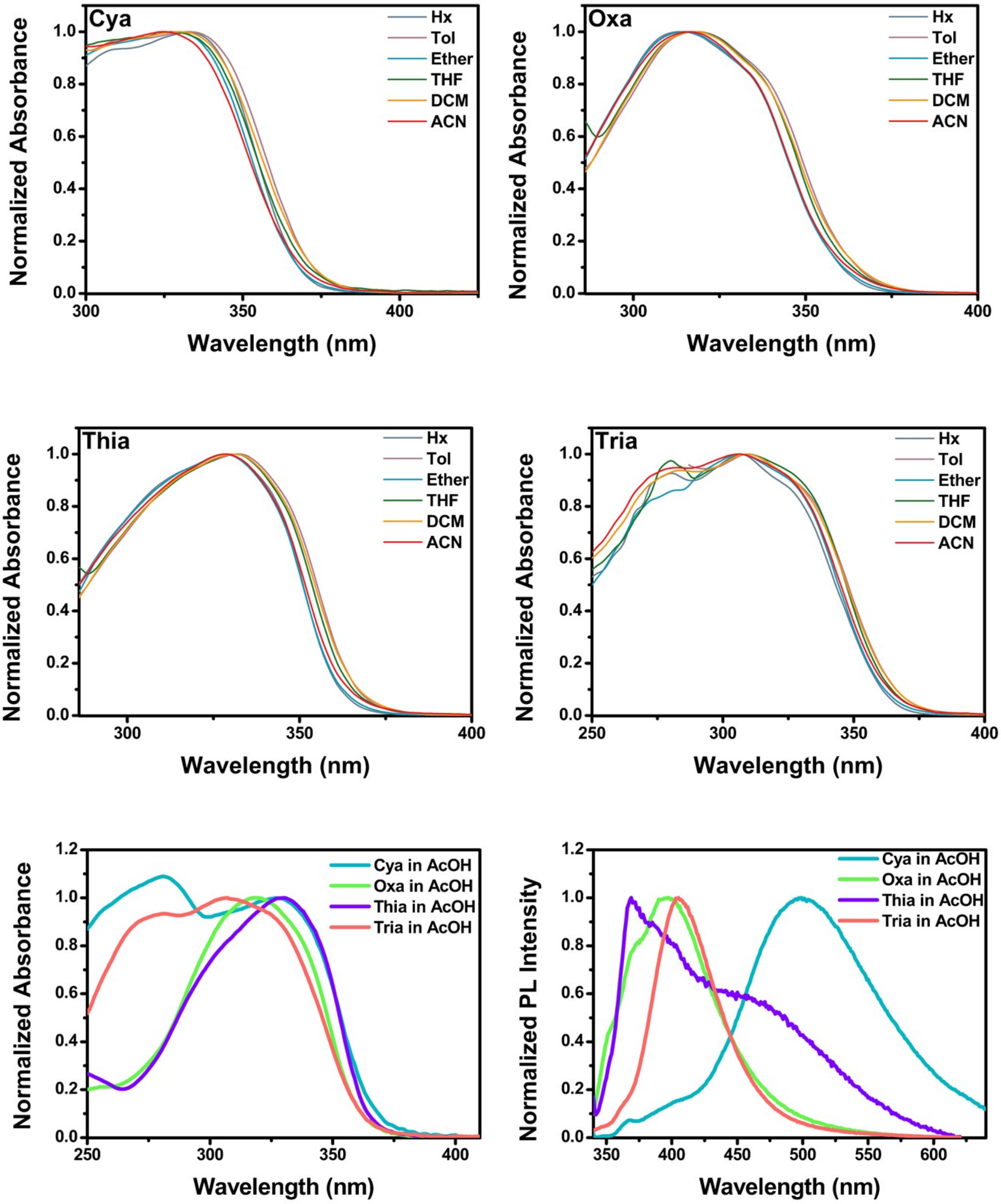

Figure S14. UV-vis absorption spectra of **Cya**–**Tria** in various solvents at room temperature. UV-vis absorption and emission spectra of **Cya**–**Tria** in the acetic acid solution.

Table S2. Spectroscopic parameters of **Cya**–**Tria** in various solvents

dyads	Solvents	λ_{max} abs (nm)	λ_{max} em (nm)	Stokes shift (cm^{-1})
Cya	*n*-Hexane	333	377	3505
	Toluene	333	409	5580
	Ether	328	434	7446
	THF	328	363, 482	9741
	DCM	329	506	10632
	ACN	325	360, 567	13132
Oxa	*n*-Hexane	314, 335	373	3041
	Toluene	318, 338	413	5373
	Ether	315, 336	361, 444	7239
	THF	318, 338	366, 494	9343
	DCM	318, 338	368, 517	10243
	ACN	316, 337	365, 596	12895
Thia	*n*-Hexane	329, 345	374	2248
	Toluene	332, 346	423	5261
	Ether	328, 343	456	7225
	THF	331, 346	369, 513	9408
	DCM	331, 346	375, 541	10417
	ACN	329, 345	365, 630	13112
Tria	*n*-Hexane	307, 327	340, 391	5006
	Toluene	310, 335	343, 450	7628
	Ether	306, 329	389, 491	10028
	THF	309, 332	404, 559	12231
	DCM	309, 330	405, 591	13382
	ACN	306, 333	350, 427, 722	16180

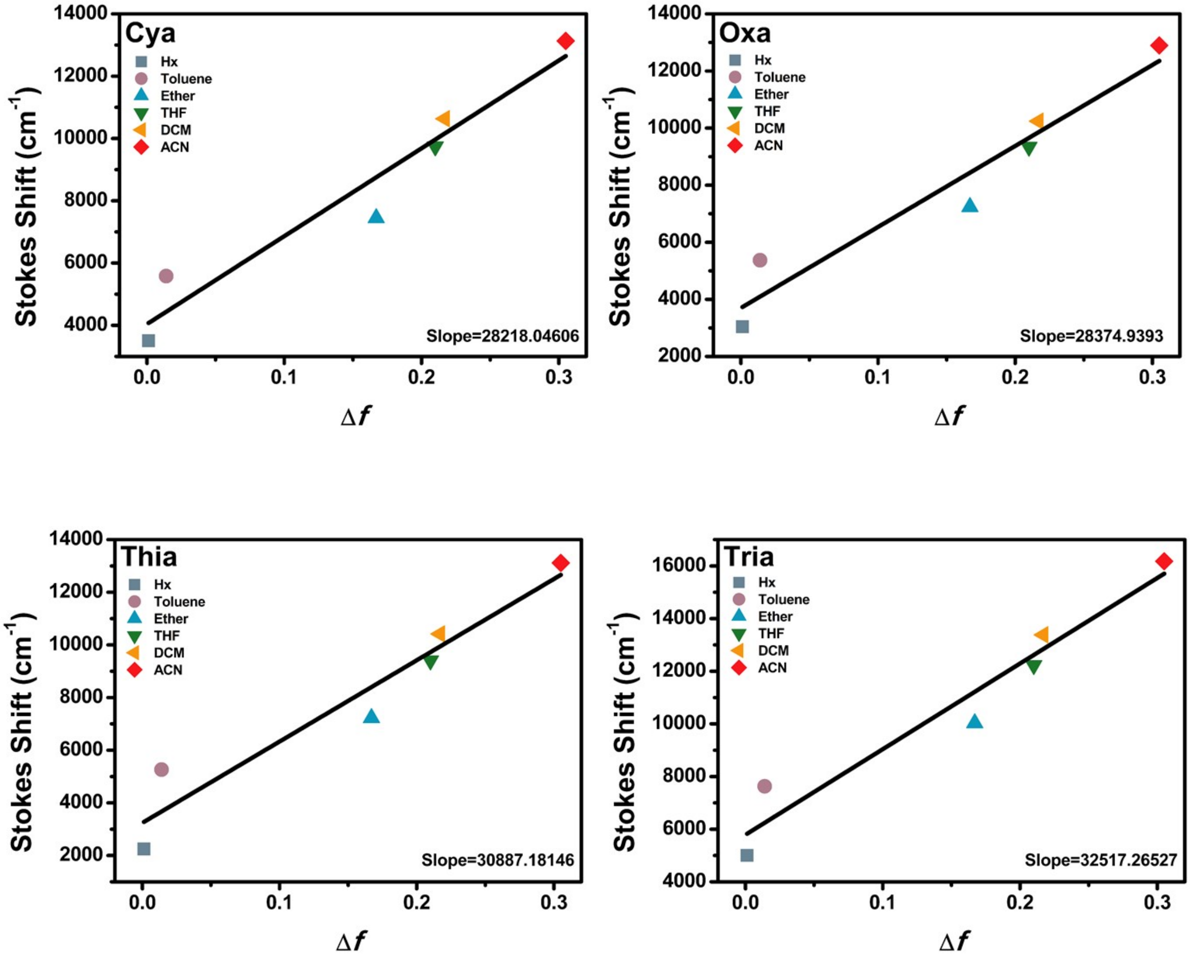

Figure S15. Lippert-Mataga plots for **Cya–Tria**.

Table S3. Dipole moment values of **Cya–Tria** in the ground and excited states

Dyads	$\Delta\mu$	μ_g	μ_e
Cya	34.49 D	5.92 D	40.41 D
Oxa	59.71 D	1.98 D	61.69 D
Thia	64.21 D	1.52 D	65.73 D
Tria	72.45 D	0.94 D	73.39 D

DFT/TD-DFT Calculation Details

All the calculations were performed on the platform of the Gaussian 16 package.[1] The ground-state geometry of all dyads has been optimized at the density function theory (DFT) level. Full geometry optimizations in their ground state were performed using the B3LYP functional[2-5] and the 6-31G[6,7] basis set for all atoms. No charge and no symmetry constraints were applied during the geometry optimizations. The nature of the stationary points located was further checked by computations of harmonic vibrational frequencies at the same level of theory. As well as, all of the Cartesian coordinates for optimized structure of all dyads are also summarized in Table S5–S8. The Isodensity plots (isodensity contour = 0.045 a.u.) of the selected frontier orbitals (HOMO-3, HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2, LUMO+3) were visualized by Chem3D Ultra and GaussView 5.0 program (Figure S16–S19). The excitation energies and oscillator strengths for the lowest 100 singlet–singlet transitions at the optimized geometry in the ground state were obtained in TD-DFT calculations using the same basis set and functional as for the ground state. The simulated absorption spectra were obtained by the GaussSum program based on TD-DFT results (Figure S20–S23). To reduce the meaningless features, only 20 singlet–singlet transitions are summarized in Table S9–S12.

Table S4. The number of imaginary frequencies, total energies, and dipole moments for the dyads **Cya–Tria** as obtained in the geometry optimizations at B3LYP/6-31G method

Entry	Number of imaginary frequencies	Total energies (Eh) (Hartrees)	Ground state dipole moment (field-independent basis, Debye)
Cya	0	-1304.09131610	5.92
Oxa	0	-1610.39647096	1.98
Thia	0	-1933.36904757	1.52
Tria	0	-1953.17801918	0.94

Table S5. Cartesian coordinates for optimized structure for **Cya**
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	X	Y	Z	Atom	X	Y	Z
C	1.624835	-1.7702	0.034847	C	7.38388	1.332572	0.010013
C	1.865892	-3.15499	0.039871	C	7.441032	0.134916	-0.72192
C	3.168173	-3.64948	0.039289	C	6.360594	-0.73835	-0.71011
C	4.25573	-2.77896	0.038061	C	8.494331	2.238449	0.001479
C	4.04861	-1.38976	0.03672	N	9.396026	2.973988	-0.00543
C	2.731602	-0.90698	0.032846	H	1.02795	-3.84429	0.070758
C	0.242428	-1.23457	0.022342	H	3.337019	-4.72218	0.059111
C	-0.09528	-0.06296	0.721092	H	5.266062	-3.17467	0.068331
C	-1.39115	0.439169	0.718894	H	2.562468	0.163483	-0.0268
C	-2.40809	-0.20855	-0.0031	H	0.661417	0.44361	1.312845
C	-2.08036	-1.37711	-0.71167	H	-1.62596	1.332322	1.287456
C	-0.78442	-1.87863	-0.68897	H	-2.8457	-1.88308	-1.28992
C	5.197922	-0.45065	0.02705	H	-0.55619	-2.76652	-1.27107
N	-3.72821	0.30304	-0.01634	H	-5.94248	0.497294	-1.49755
C	-4.84112	-0.58421	0.005456	H	-7.88865	-1.02858	-1.44684
C	-3.95173	1.708534	-0.05201	H	-7.89576	-3.00245	0.070517
C	-5.94705	-0.35662	-0.82852	H	-5.93492	-3.41618	1.547839
C	-7.04081	-1.21922	-0.79516	H	-4.00405	-1.87096	1.51787
C	-7.04473	-2.32877	0.052342	H	-5.51921	1.66263	1.425365
C	-5.9424	-2.56184	0.877038	H	-5.927	4.101254	1.35053
C	-4.85187	-1.69463	0.864416	H	-4.57607	5.553235	-0.15453
C	-4.9358	2.291713	0.761511	H	-2.82437	4.526707	-1.59542
C	-5.16147	3.665912	0.714663	H	-2.44078	2.083998	-1.54198
C	-4.40213	4.482093	-0.12594	H	4.280989	0.983445	1.352917
C	-3.41712	3.905416	-0.93018	H	6.185567	2.554521	1.323939
C	-3.19667	2.529832	-0.90422	H	8.327883	-0.09674	-1.30205
C	5.156609	0.7516	0.755485	H	6.406261	-1.64699	-1.30148
C	6.229016	1.634754	0.750478				

Table S6. Cartesian coordinates for optimized structure for **Oxa**
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.76296	-2.41045	0.076088	C	8.260053	1.663569	0.397263
C	-0.80997	-3.81448	0.118373	C	8.83923	0.679294	-0.41765
C	0.365039	-4.56265	0.133853	N	7.884089	-0.29485	-0.69142
C	1.606666	-3.93139	0.112289	C	8.935837	2.782209	0.858715
C	1.688489	-2.52946	0.07273	C	10.27096	2.889136	0.460145
C	0.495963	-1.79053	0.052647	C	10.87715	1.916898	-0.35669
C	-2.00772	-1.60498	0.04687	C	10.17603	0.79971	-0.80835
C	-2.09856	-0.37313	0.717135	H	-1.77067	-4.31767	0.165869
C	-3.26558	0.381699	0.699951	H	0.312756	-5.64652	0.182287
C	-4.39398	-0.06268	-0.00932	H	2.515604	-4.52322	0.154712
C	-4.31267	-1.28914	-0.68976	H	0.547966	-0.71005	-0.03621
C	-3.1456	-2.04319	-0.65196	H	-1.25263	-0.01745	1.297806
C	3.004738	-1.84483	0.040323	H	-3.31306	1.317288	1.24654
N	-5.58393	0.706486	-0.03759	H	-5.16664	-1.64202	-1.2577
C	-6.85205	0.063926	0.022631	H	-3.10354	-2.97262	-1.21199
C	-5.51675	2.125039	-0.12644	H	-7.7359	1.298086	-1.50644
C	-7.90202	0.483563	-0.8095	H	-9.94746	0.197302	-1.39036
C	-9.14604	-0.14003	-0.73928	H	-10.3293	-1.6879	0.190675
C	-9.36071	-1.19991	0.14388	H	-8.46993	-2.44264	1.664667
C	-8.31566	-1.62473	0.966658	H	-6.26898	-1.31939	1.568684
C	-7.07352	-0.99547	0.917056	H	-7.0588	2.45588	1.341614
C	-6.35986	2.927195	0.658878	H	-6.95956	4.921373	1.175396
C	-6.29986	4.31576	0.560583	H	-5.34189	6.010511	-0.37264
C	-5.39061	4.928207	-0.30403	H	-3.83818	4.594714	-1.76332
C	-4.5451	4.13286	-1.08	H	-3.96164	2.129335	-1.61833
C	-4.61036	2.743214	-1.00262	H	3.946895	-3.3047	-1.24055
C	4.08658	-2.38645	-0.67891	H	6.14675	-2.16966	-1.27483
C	5.320117	-1.7511	-0.71126	H	4.583738	0.935764	1.243912
C	5.512734	-0.54317	-0.02076	H	2.401945	-0.21025	1.31224
C	4.4424	0.008431	0.700005	H	8.458191	3.524845	1.487755
C	3.211213	-0.63615	0.727623	H	10.85368	3.743765	0.789474
C	6.815398	0.108008	-0.0684	H	11.91745	2.043175	-0.64048
O	6.957239	1.296676	0.62245	H	10.64012	0.048408	-1.43802

Table S7. Cartesian coordinates for optimized structure for **Thia**
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	X	Y	Z	Atom	X	Y	Z
C	-1.03333	-2.40433	0.081968	C	8.503252	1.650239	0.325734
C	-1.07487	-3.80887	0.110588	C	8.692451	0.48791	-0.46272
C	0.10314	-4.5522	0.132586	N	7.583744	-0.32469	-0.59682
C	1.342225	-3.9156	0.131373	C	9.540117	2.559264	0.544569
C	1.41858	-2.51301	0.105899	C	10.77782	2.294246	-0.03639
C	0.22312	-1.77899	0.078816	C	10.9792	1.145182	-0.82069
C	-2.28109	-1.60369	0.045871	C	9.948065	0.240545	-1.0386
C	-2.38449	-0.37812	0.725755	H	-2.03385	-4.31654	0.142289
C	-3.55429	0.37222	0.701968	H	0.054956	-5.63668	0.17025
C	-4.67288	-0.07042	-0.02378	H	2.253109	-4.50403	0.178796
C	-4.57895	-1.29062	-0.7138	H	0.271453	-0.69753	0.000444
C	-3.40929	-2.0403	-0.66943	H	-1.5466	-0.02415	1.318977
C	2.732004	-1.82276	0.095433	H	-3.61167	1.302816	1.256076
N	-5.86544	0.694377	-0.05885	H	-5.42503	-1.64195	-1.29437
C	-7.1317	0.046618	-0.01933	H	-3.3572	-2.96462	-1.23701
C	-5.8028	2.113941	-0.13412	H	-8.00227	1.291465	-1.54734
C	-8.17347	0.470011	-0.85982	H	-10.2109	0.18162	-1.46716
C	-9.41589	-0.15871	-0.80983	H	-10.6041	-1.71926	0.092176
C	-9.6369	-1.22736	0.06113	H	-8.75928	-2.48061	1.580949
C	-8.59992	-1.65585	0.892198	H	-6.56155	-1.3486	1.520832
C	-7.35964	-1.02168	0.862819	H	-7.36154	2.425521	1.320455
C	-6.65728	2.905703	0.649459	H	-7.27013	4.892823	1.17767
C	-6.60166	4.295329	0.56439	H	-5.64049	6.002118	-0.34327
C	-5.68572	4.919059	-0.28499	H	-4.11669	4.604765	-1.73072
C	-4.82897	4.134021	-1.05913	H	-4.232	2.137692	-1.60927
C	-4.88962	2.743491	-0.995	H	2.108291	-0.19822	1.370661
C	2.925406	-0.61833	0.792922	H	4.268042	0.953597	1.343573
C	4.155265	0.029265	0.784188	H	5.892797	-2.12213	-1.17891
C	5.242868	-0.50534	0.076369	H	3.700533	-3.26758	-1.18226
C	5.057559	-1.71098	-0.62345	H	9.389693	3.447672	1.149187
C	3.826883	-2.35255	-0.612	H	11.59845	2.987646	0.12045
C	6.555923	0.147185	0.042674	H	11.95478	0.964089	-1.26128
S	6.851154	1.69035	0.904876	H	10.08793	-0.65053	-1.64129

Table S8. Cartesian coordinates for optimized structure for **Tria**

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Atom	X	Y	Z
C	2.622604	-2.48719	-0.74996
C	2.715645	-3.82759	-1.16219
C	1.565893	-4.57358	-1.41186
C	0.304483	-4.00193	-1.2611
C	0.176847	-2.66359	-0.85355
C	1.344227	-1.92721	-0.60183
C	3.839799	-1.68779	-0.46938
C	3.905497	-0.31961	-0.78366
C	5.046419	0.432563	-0.52959
C	6.172103	-0.15647	0.07003
C	6.115775	-1.52197	0.395409
C	4.975206	-2.26792	0.12174
C	-1.16101	-2.04473	-0.681
N	7.334827	0.607875	0.340087
C	8.624799	0.039305	0.148069
C	7.217133	1.946761	0.807212
C	9.642317	0.24926	1.09237
C	10.90784	-0.29927	0.895106
C	11.1768	-1.07851	-0.23178
C	10.16421	-1.29588	-1.16825
C	8.900793	-0.73634	-0.98934
C	8.049004	2.954593	0.294077
C	7.938849	4.262291	0.762245
C	6.990204	4.592242	1.732112
C	6.155889	3.593444	2.237969
C	6.270896	2.279191	1.789797
C	-1.39117	-0.70276	-1.03287
C	-2.64297	-0.12179	-0.87254
C	-3.71384	-0.8656	-0.35347
C	-3.49357	-2.20577	-8.8E-05
C	-2.23981	-2.78228	-0.16136
C	-5.04912	-0.24892	-0.18233
N	-5.19883	1.035909	-0.54147
C	-6.42543	1.55159	-0.3695
N	-7.46814	0.867912	0.126952
C	-7.22487	-0.40942	0.459197
N	-6.03313	-1.01023	0.321972
C	-8.34544	-1.20805	1.01351
C	-6.64309	2.968187	-0.75246
C	-7.90559	3.560633	-0.59397
C	-8.10791	4.890288	-0.95421
C	-7.05423	5.644072	-1.47637
C	-5.7951	5.060984	-1.63684
C	-5.58891	3.731639	-1.27772
C	-8.1483	-2.54813	1.381443
C	-9.20116	-3.29602	1.901807
C	-10.4621	-2.71663	2.061061
C	-10.6656	-1.38355	1.696943
C	-9.61514	-0.63239	1.176369
H	3.69283	-4.27593	-1.31228
H	1.654118	-5.60372	-1.74488
H	-0.58408	-4.58324	-1.48634
H	1.255042	-0.91071	-0.23206
H	3.06182	0.156832	-1.27401
H	5.075635	1.481277	-0.80474
H	6.967695	-1.99205	0.874607
H	4.95083	-3.31408	0.411897
H	9.434202	0.843086	1.975999
H	11.68345	-0.12677	1.635817
H	12.16205	-1.51008	-0.37843
H	10.36061	-1.89311	-2.05411
H	8.121626	-0.89596	-1.72704
H	8.778589	2.705404	-0.46907
H	8.590499	5.029752	0.354401
H	6.902538	5.613648	2.089196
H	5.418469	3.833157	2.998702
H	5.630296	1.503883	2.196389
H	-0.58311	-0.11812	-1.46149
H	-2.8115	0.910638	-1.15496
H	-4.3157	-2.78061	0.40947
H	-2.08356	-3.81228	0.143914
H	-8.71463	2.965254	-0.18788
H	-9.08832	5.340037	-0.82794
H	-7.21361	6.681272	-1.75701
H	-4.97335	5.643708	-2.04253
H	-4.61716	3.267595	-1.3973
H	-7.16549	-2.98577	1.253044
H	-9.03893	-4.33216	2.183832
H	-11.2826	-3.30136	2.467145
H	-11.6445	-0.92947	1.819193
H	-9.75994	0.402535	0.890209

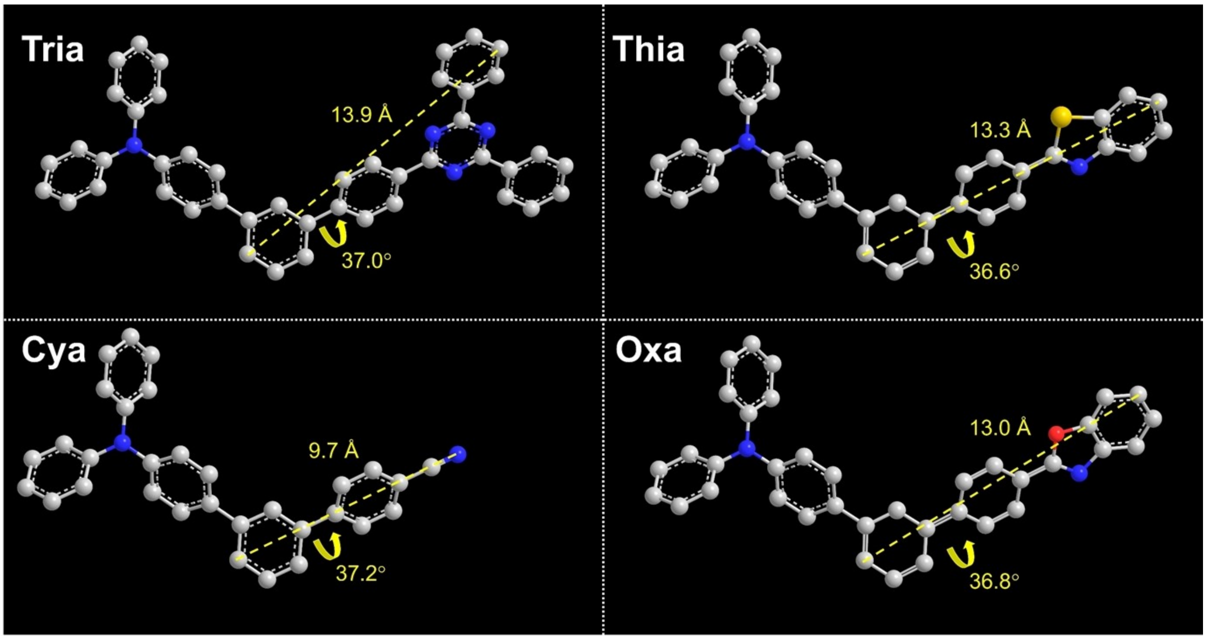

Figure S16. Optimized structure of dyads. The gray, blue, red, and yellow balls refer to C, N, O, and S atoms.

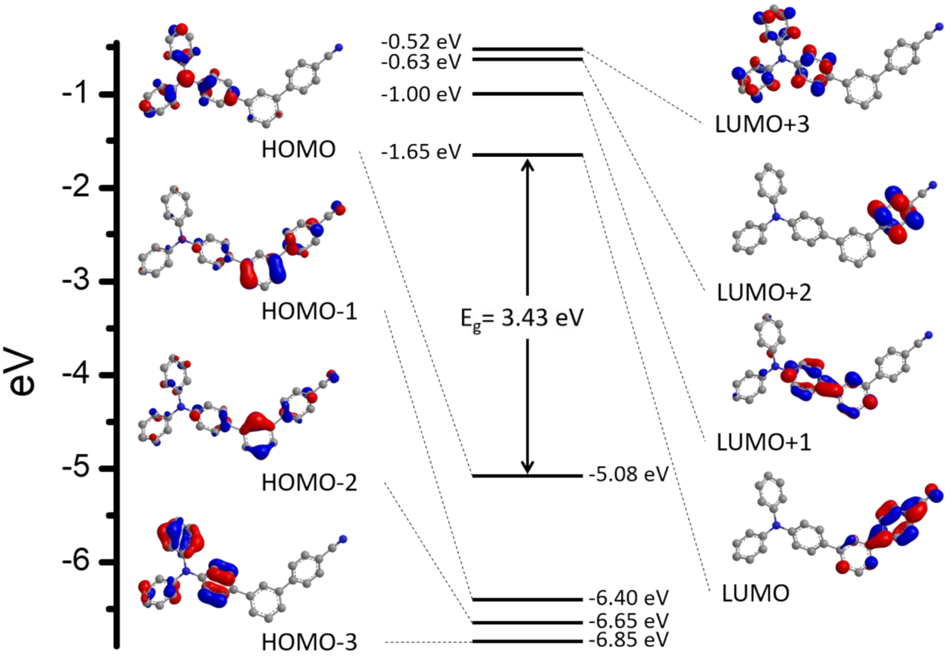

Figure S17. Energy levels and isodensity plots (isodensity contour = 0.045 a.u.) for selected occupied and unoccupied molecular orbitals of **Cya** obtained by DFT calculations.

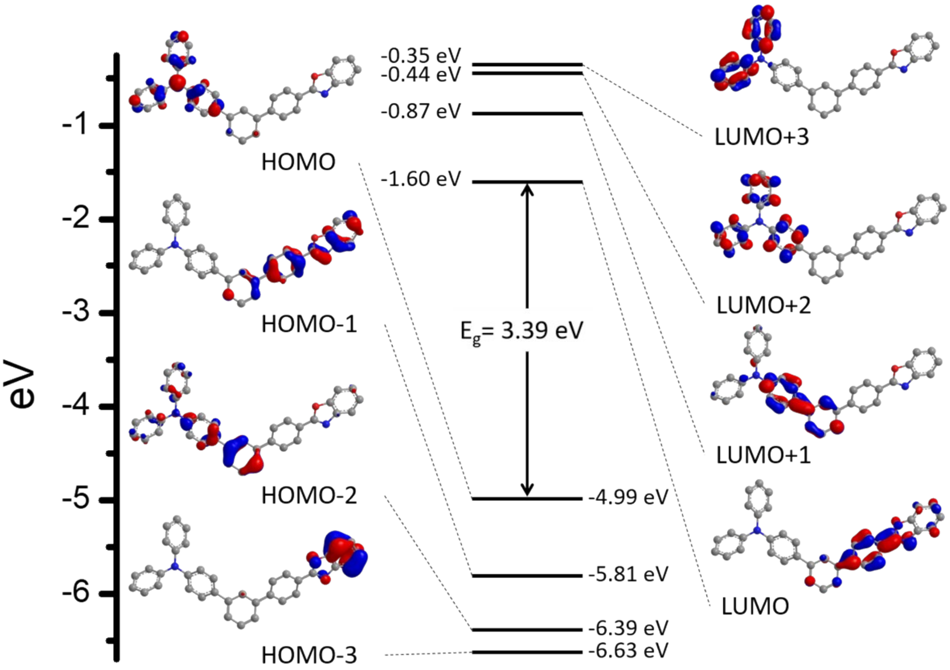

Figure S18. Energy levels and isodensity plots (isodensity contour = 0.045 a.u.) for selected occupied and unoccupied molecular orbitals of **Oxa** obtained by DFT calculations.

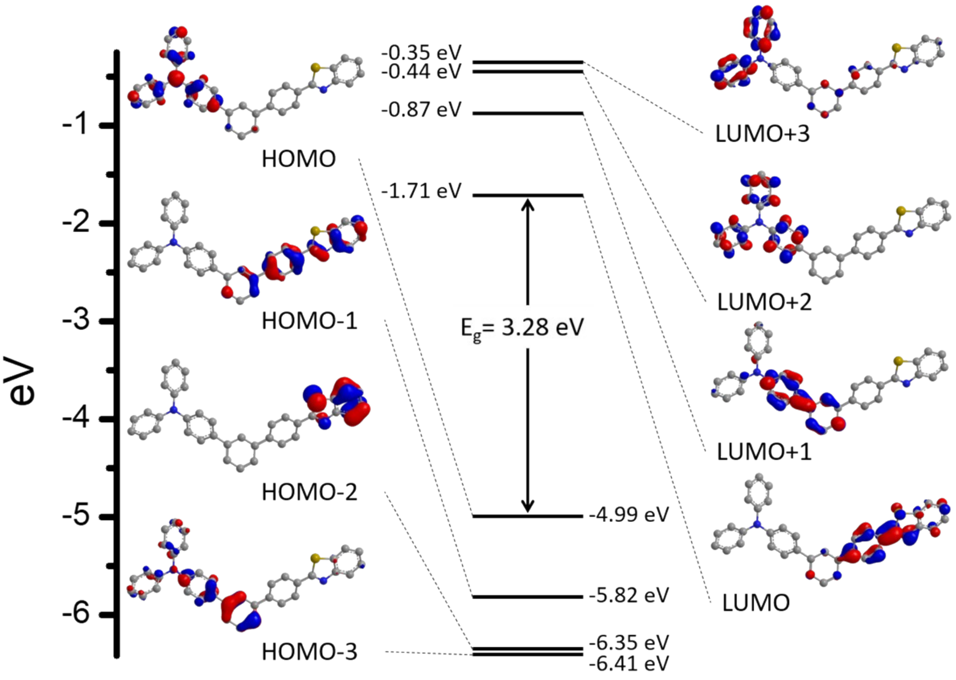

Figure S19. Energy levels and isodensity plots (isodensity contour = 0.045 a.u.) for selected occupied and unoccupied molecular orbitals of **Thia** obtained by DFT calculations.

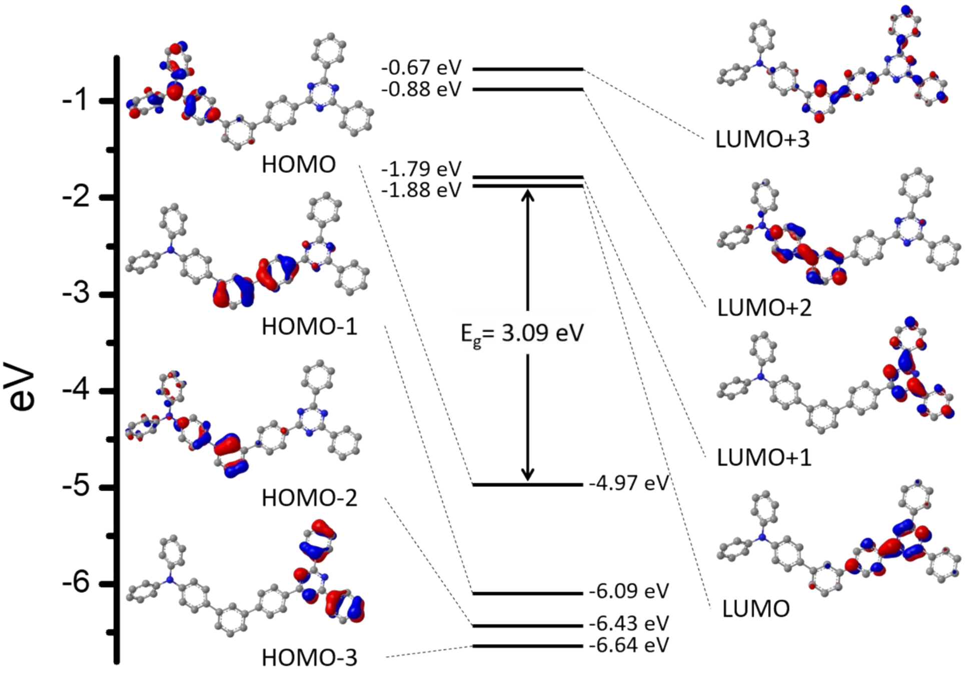

Figure S20. Energy levels and isodensity plots (isodensity contour = 0.045 a.u.) for selected occupied and unoccupied molecular orbitals of **Tria** obtained by DFT calculations.

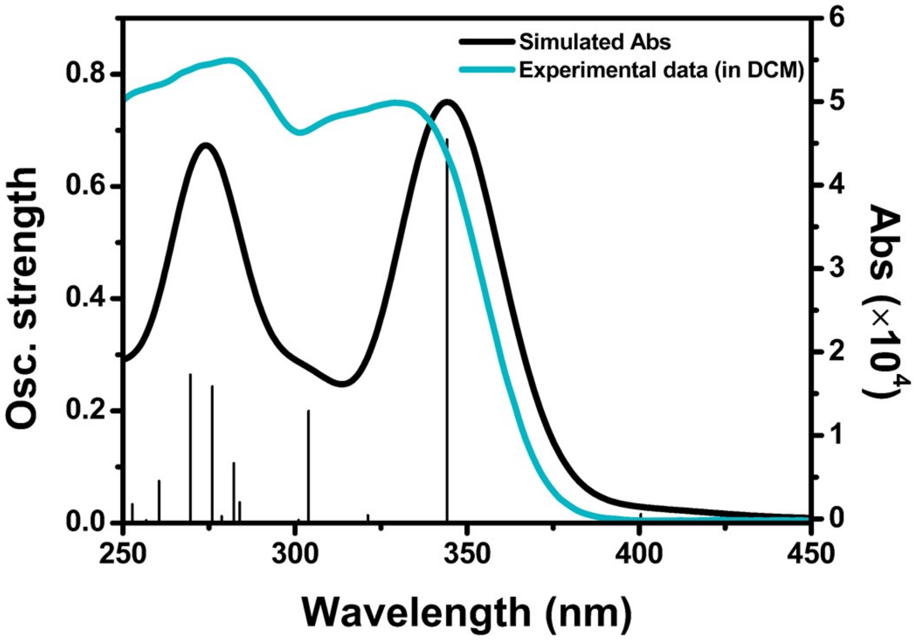

Figure S21. Electronic transition and simulated absorption spectra of **Cya** in the ground state geometry obtained by TD-DFT calculations.

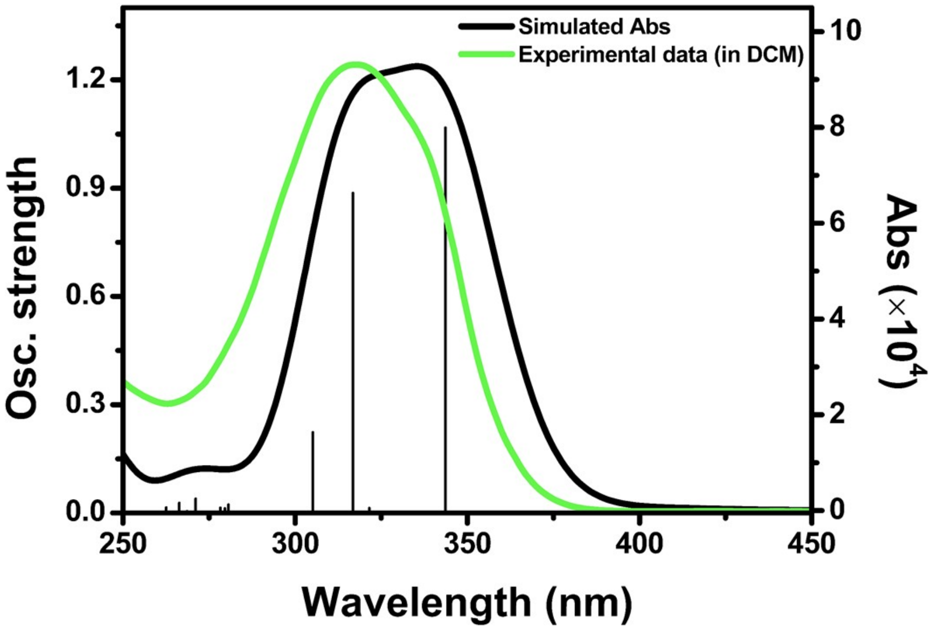

Figure S22. Electronic transition and simulated absorption spectra of **Oxa** in the ground state geometry obtained by TD-DFT calculations.

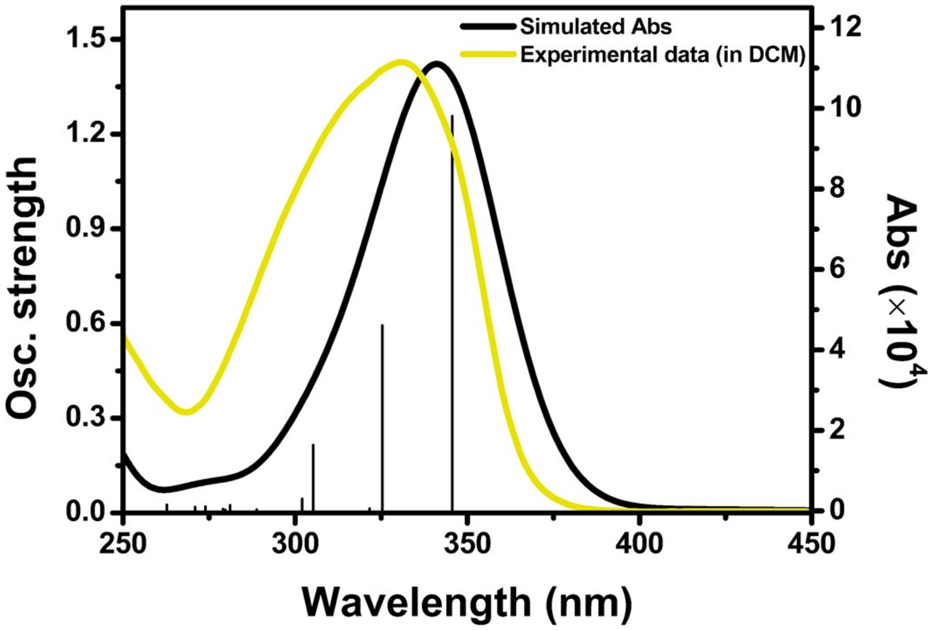

Figure S23. Electronic transition and simulated absorption spectra of **Thia** in the ground state geometry obtained by TD-DFT calculations.

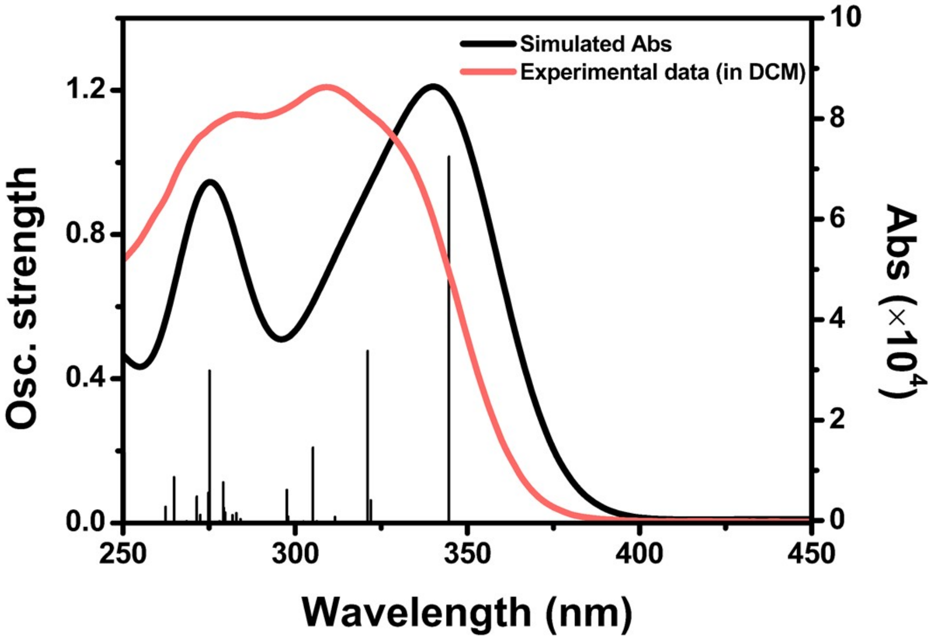

Figure S24. Electronic transition and simulated absorption spectra of **Tria** in the ground state geometry obtained by TD-DFT calculations.

Table S9. TD-DFT calculation: Transition assignment of **Cya**

No.	Excitation Energy (cm^{-1})	Wavelength (nm)	Oscillator strength	Assignment
1	24969.48448	400.49	0.0156	HOMO->LUMO (99%)
2	29055.51744	344.17	0.6835	HOMO->L+1 (97%)
3	31136.44224	321.17	0.0139	HOMO->L+3 (96%)
4	32897.16272	303.98	0.1996	HOMO->L+4 (97%)
5	33214.1408	301.08	0.0052	HOMO->L+2 (99%)
6	35220.05552	283.93	0.0368	H-2->LUMO (17%), H-1->LUMO (48%), HOMO->L+5 (13%)
7	35431.37424	282.24	0.1068	H-1->LUMO (19%), HOMO->L+5 (23%), HOMO->L+6 (47%)
8	35883.8544	278.68	0.0121	HOMO->L+7 (90%)
9	36233.90144	275.98	0.2437	H-2->LUMO (22%), H-1->LUMO (17%), HOMO->L+5 (26%), HOMO->L+6 (22%)
10	37090.46816	269.61	0.2645	H-2->LUMO (40%), HOMO->L+5 (31%), HOMO->L+6 (11%)
11	38386.61008	260.51	0.075	H-1->L+1 (15%), HOMO->L+8 (78%)
12	38939.91024	256.81	0.0047	H-7->LUMO (10%), H-3->LUMO (68%)
13	38960.8808	256.67	0.003	H-7->LUMO (33%), H-3->LUMO (21%), H-1->L+2 (25%)
14	39570.64016	252.71	0.0334	H-4->LUMO (54%), H-2->LUMO (11%), H-1->L+1 (17%)
15	40259.4424	248.39	0.1246	H-4->LUMO (37%), H-1->L+1 (44%)
16	41410.40352	241.49	0.0015	H-6->LUMO (25%), H-5->LUMO (62%)
17	41730.60784	239.63	0.0985	H-2->L+1 (75%)
18	41954.02496	238.36	0.0127	H-3->L+1 (39%), H-1->L+3 (22%)
19	42091.94672	237.58	0.0012	H-6->LUMO (70%), H-5->LUMO (29%)
20	43137.24848	231.82	0.0493	H-8->LUMO (58%), H-4->L+1 (13%)

Table S10. TD-DFT calculation: Transition assignment of **Oxa**

No.	Excitation Energy (cm^{-1})	Wavelength (nm)	Oscillator strength	Assignment
1	24858.1792	402.28	0.0076	HOMO->LUMO (99%)
2	29101.49136	343.63	1.0675	H-1->LUMO (11%), HOMO->L+1 (87%)
3	31100.14704	321.54	0.0135	HOMO->L+2 (96%)
4	31567.14528	316.79	0.8867	H-1->LUMO (87%), HOMO->L+1 (11%)
5	32772.14592	305.14	0.2233	HOMO->L+3 (94%)
6	34545.77136	289.47	0.0028	H-2->LUMO (26%), H-1->L+1 (13%), HOMO->L+4 (41%)
7	35174.88816	284.29	0.003	H-2->LUMO (44%), HOMO->L+4 (30%), HOMO->L+6 (14%)
8	35631.40112	280.65	0.0233	HOMO->L+4 (18%), HOMO->L+5 (14%), HOMO->L+6 (52%)
9	35766.09664	279.59	0.0126	HOMO->L+7 (86%)
10	35934.66768	278.28	0.0145	HOMO->L+5 (70%)
11	36215.35056	276.13	0.0033	H-3->LUMO (77%)
12	36883.18224	271.13	0.0396	H-8->LUMO (11%), H-2->LUMO (15%), H-1->L+1 (54%)
13	37229.19648	268.61	0.0051	H-8->LUMO (43%), H-1->L+1 (18%), H-1->L+4 (10%), H-1->L+5 (16%)
14	37544.56144	266.35	0.0277	H-4->LUMO (70%)
15	38088.98944	262.54	0.0153	HOMO->L+8 (46%), HOMO->L+9 (35%)
16	38885.87072	257.16	0.0006	H-5->LUMO (90%)
17	39723.88656	251.74	0.0003	H-6->LUMO (89%)
18	40095.71072	249.40	0.0024	HOMO->L+8 (37%), HOMO->L+9 (50%)
19	40689.33888	245.76	0.0097	H-1->L+2 (79%)
20	41124.88128	243.16	0.1368	H-2->L+1 (61%), H-1->L+4 (10%)

Table S11. TD-DFT calculation: Transition assignment of **Thia**

No.	Excitation Energy (cm^{-1})	Wavelength (nm)	Oscillator strength	Assignment
1	24053.23232	415.74	0.0052	HOMO->LUMO (99%)
2	28937.75968	345.57	1.257	H-1->LUMO (23%), HOMO->L+1 (76%)
3	30740.42128	325.30	0.5938	H-1->LUMO (74%), HOMO->L+1 (22%)
4	31094.50112	321.60	0.014	HOMO->L+2 (93%)
5	32763.27376	305.22	0.2151	HOMO->L+3 (70%), HOMO->L+4 (27%)
6	33108.48144	302.04	0.045	H-2->LUMO (88%)
7	34041.67136	293.76	0.0035	H-3->LUMO (36%), HOMO->L+3 (12%), HOMO->L+4 (29%)
8	34621.588	288.84	0.011	H-3->LUMO (46%), HOMO->L+3 (14%), HOMO->L+4 (30%)
9	35572.52224	281.12	0.0245	HOMO->L+5 (10%), HOMO->L+7 (71%)
10	35746.7392	279.75	0.0095	HOMO->L+5 (14%), HOMO->L+8 (73%)
11	35837.88048	279.03	0.0126	HOMO->L+5 (57%), HOMO->L+8 (21%)
12	36502.48592	273.95	0.0201	H-8->LUMO (52%), H-1->L+1 (13%), H-1->L+5 (10%)
13	36852.53296	271.35	0.0013	H-4->LUMO (41%), H-1->L+1 (19%)
14	36908.1856	270.94	0.0188	H-4->LUMO (28%), H-1->L+1 (48%)
15	37732.48992	265.02	0.0007	H-11->LUMO (94%)
16	37826.85744	264.36	0.0004	HOMO->L+6 (89%)
17	38055.11392	262.78	0.0259	HOMO->L+9 (86%)
18	38125.28464	262.29	0.0013	H-5->LUMO (80%), H-4->LUMO (12%)
19	38911.68064	256.99	0.0005	H-6->LUMO (86%)
20	40564.32208	246.52	0.0044	H-7->LUMO (17%), H-1->L+2 (47%)

Table S12. TD-DFT calculation: Transition assignment of **Tria**

No.	Excitation Energy (cm^{-1})	Wavelength (nm)	Oscillator strength	Assignment
1	22782.90032	438.93	0.0035	HOMO->LUMO (99%)
2	23964.51072	417.28	0	HOMO->L+1 (100%)
3	29011.15664	344.69	1.0159	H-1->LUMO (11%), HOMO->L+2 (81%)
4	30767.84432	325.01	0.0003	H-1->L+1 (87%)
5	31059.01248	321.97	0.0632	HOMO->L+4 (81%)
6	31147.73408	321.05	0.4771	H-1->LUMO (75%), HOMO->L+2 (11%)
7	32093.0224	311.59	0.017	HOMO->L+3 (83%)
8	32647.93568	306.30	0.0049	H-13->L+1 (21%), H-12->LUMO (71%)
9	32766.5	305.19	0.2088	HOMO->L+5 (96%)
10	33070.57312	302.38	0.0043	H-13->LUMO (89%)
11	33199.62272	301.21	0.0006	H-13->L+1 (72%), H-12->LUMO (21%)
12	33353.67568	299.82	0.0038	H-12->L+1 (84%)
13	33556.12224	298.01	0.0176	H-4->L+1 (12%), H-3->LUMO (63%)
14	33603.70928	297.59	0.0916	H-2->LUMO (85%)
15	35162.78976	284.39	0.0036	H-4->LUMO (77%), H-3->L+1 (12%)
16	35195.05216	284.13	0.0109	H-2->L+1 (91%)
17	35345.07232	282.92	0.0272	H-9->LUMO (51%), H-7->LUMO (19%), H-4->L+1 (16%)
18	35487.02688	281.79	0.022	HOMO->L+9 (35%), HOMO->L+10 (47%)
19	35755.61136	279.68	0.0292	HOMO->L+10 (10%), HOMO->L+11 (81%)
20	35807.2312	279.27	0.0423	H-8->LUMO (69%), H-3->L+1 (12%)

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