Supporting Information for:

Theoretical investigation on electronic, optical, and charge transport properties of 7,8,15,16-tetraazaterrylene and its derivatives with electron-attracting substituents

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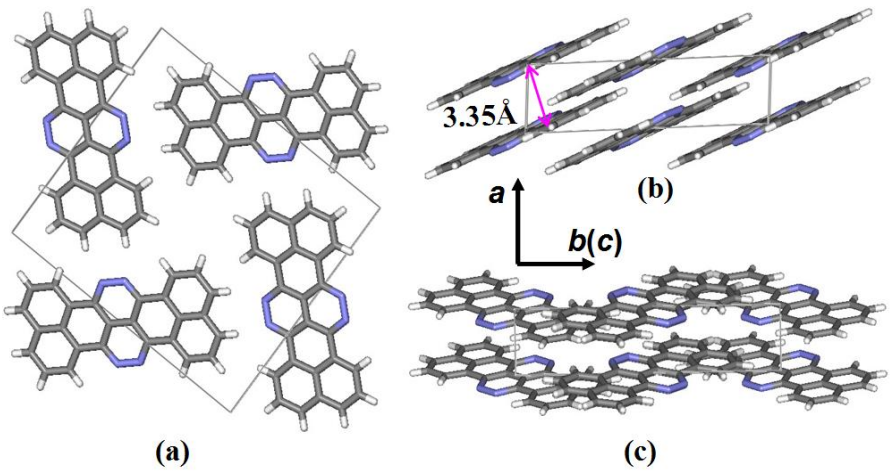

Fig.S1

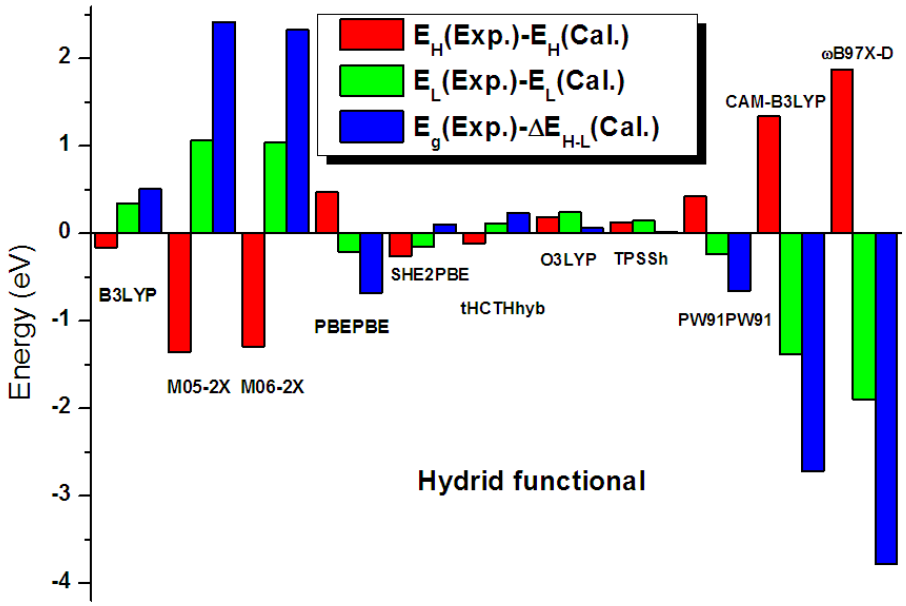

Fig.S2

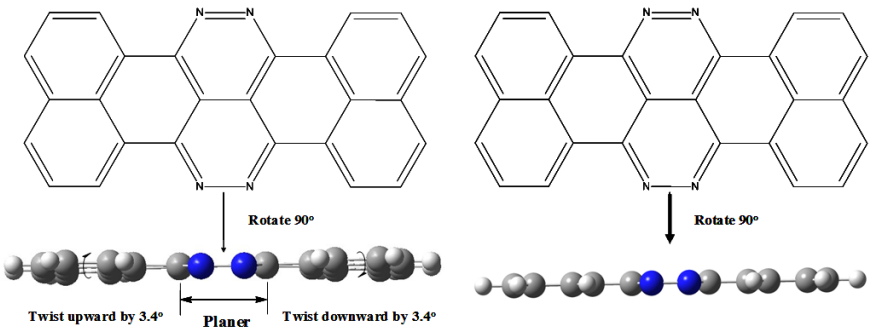

Fig.S3

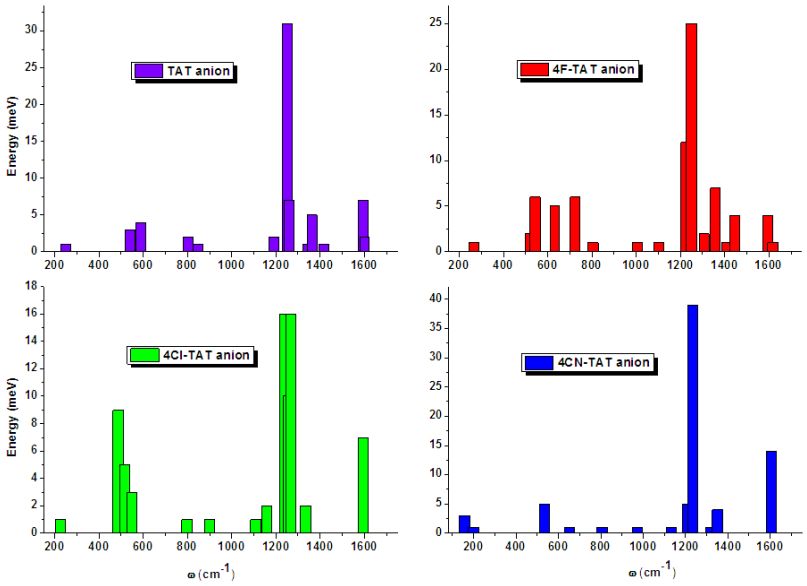

Fig.S4

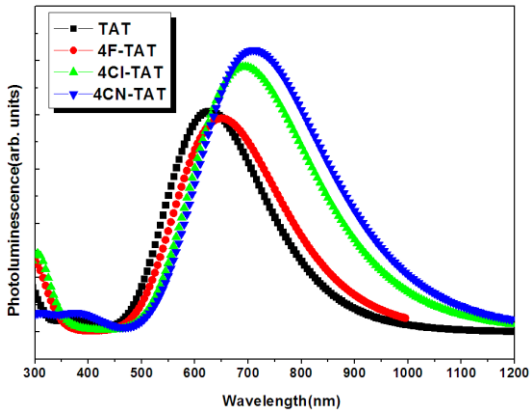

Fig.S5

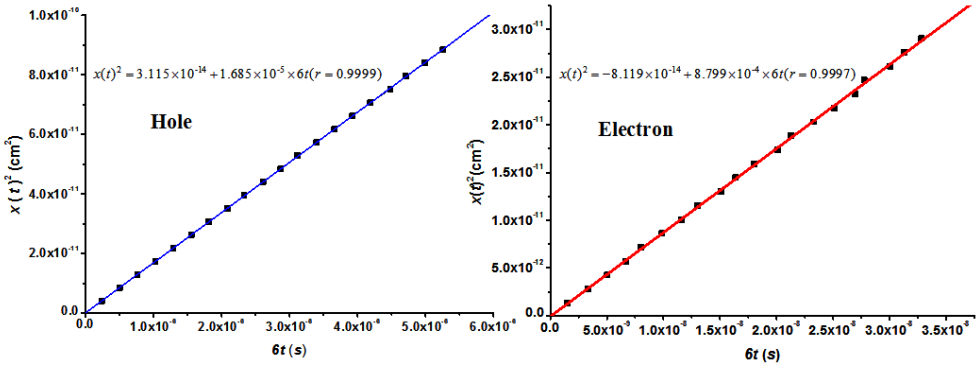

Fig.S6

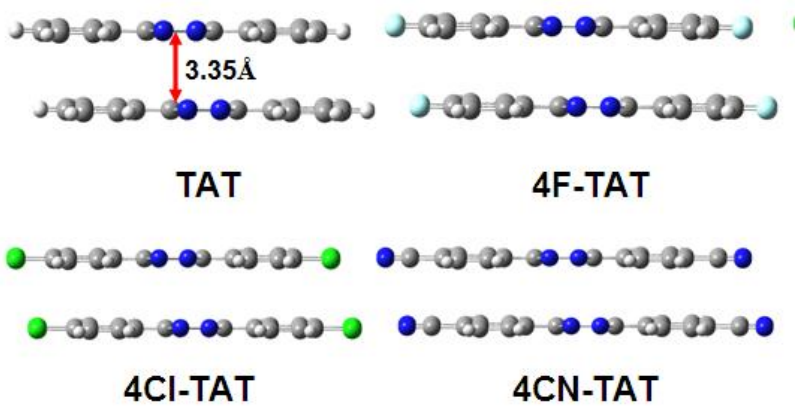

Fig.S7

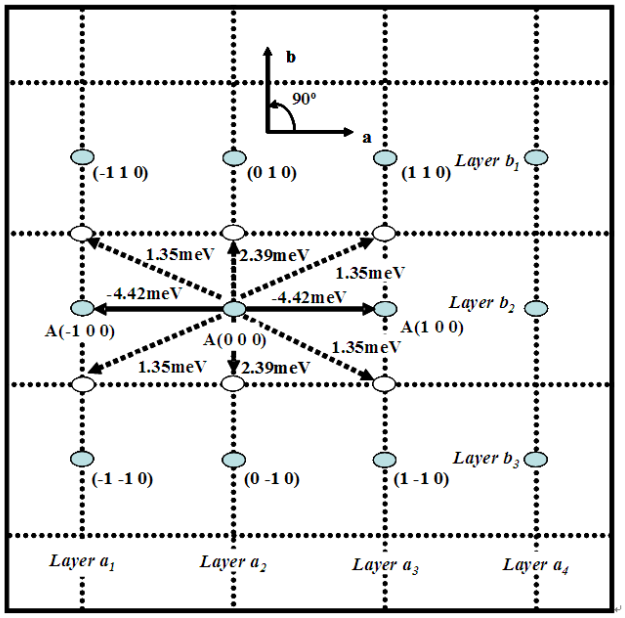

Fig.S8

Table S1

	Planer configuration		Twisted configuration	
Basis set	6-311G(d,p)	6-311++G(d,p)	6-311G(d,p)	6-311++G(d,p)
E_{HOMO}	-5.350	-5.405	-5.351	-5.410
E_{LUMO}	-3.355	-3.427	-3.271	-3.347
ΔE_{H-L}	-1.995	1.978	2.081	2.063

Table S2

	R_{1-2}	R_{1-3}	R_{2-4}	R_{3-5}	R_{4-6}	R_{5-6}	R_{4-7}	R_{7-8}	R_{8-9}	R_{7-10}	R_{10-11}
Ground state	1.399	1.375	1.390	1.418	1.433	1.436	1.459	1.339	1.339	1.413	1.389
Cation	1.387	1.388	1.406	1.417	1.431	1.433	1.440	1.359	1.316	1.409	1.390
Δ(C-G)	-0.012	0.013	0.016	-0.001	-0.002	-0.003	-0.019	0.020	-0.023	-0.004	0.001
Anion	1.396	1.377	1.399	1.416	1.437	1.443	1.449	1.359	1.322	1.411	1.396

Δ(A-G)	-0.003	0.002	0.009	-0.002	0.004	0.007	-0.010	0.020	-0.017	-0.002	0.007
Excited state	1.389	1.381	1.404	1.416	1.434	1.436	1.442	1.365	1.309	1.408	1.390
Δ(E-G)	-0.010	0.006	0.014	-0.002	0.001	0.000	-0.017	0.026	-0.030	-0.005	0.001

Table S3

	R_{1-2}	R_{1-3}	R_{2-4}	R_{3-5}	R_{4-6}	R_{5-6}	R_{4-7}	R_{7-8}	R_{8-9}	R_{7-10}	R_{10-11}
Ground state	1.391	1.379	1.382	1.434	1.436	1.454	1.463	1.335	1.338	1.409	1.385
Cation	1.379	1.394	1.398	1.435	1.433	1.451	1.442	1.356	1.313	1.404	1.387
Δ(C-G)	-0.012	0.015	0.016	0.001	-0.003	-0.003	-0.021	0.021	-0.025	-0.005	0.002
Anion	1.385	1.384	1.393	1.430	1.439	1.463	1.450	1.356	1.318	1.405	1.392
Δ(A-G)	-0.006	0.005	0.011	-0.004	0.003	0.009	-0.013	0.021	-0.020	-0.004	0.007
Excited state	1.381	1.390	1.399	1.432	1.437	1.456	1.443	1.365	1.310	1.403	1.388
Δ(E-G)	-0.010	0.011	0.017	-0.002	0.001	0.002	-0.020	0.030	-0.028	-0.006	0.003

Table S4

	R_{1-2}	R_{1-3}	R_{2-4}	R_{3-5}	R_{4-6}	R_{5-6}	R_{4-7}	R_{7-8}	R_{8-9}	R_{7-10}	R_{10-11}
Ground state	1.393	1.389	1.385	1.433	1.435	1.437	1.463	1.334	1.337	1.410	1.386
Cation	1.384	1.400	1.400	1.432	1.433	1.434	1.443	1.356	1.312	1.406	1.388
Δ(C-G)	-0.009	0.011	0.015	-0.001	-0.002	-0.003	-0.02	0.022	-0.025	-0.004	0.002
Anion	1.382	1.400	1.398	1.432	1.438	1.444	1.447	1.356	1.315	1.407	1.393
Δ(A-G)	-0.011	0.011	0.013	-0.001	0.003	0.007	-0.016	0.022	-0.022	-0.003	0.007
Excited state	1.385	1.396	1.395	1.433	1.437	1.439	1.438	1.359	1.359	1.412	1.396
Δ(E-G)	-0.008	0.007	0.010	0.000	0.002	0.002	-0.025	0.025	0.022	0.002	0.010

Table S5

	Compound	λ_{cal}/nm	*f*	λ_{exp}/nm	Main configuration
Absorption					
	TAT	555.0	0.9695	537.4[a]	HOMO→LUMO(100%)
		352.3	0.0554		HOMO-3→LUMO(92%)
		285.6	0.0441		HOMO→LUMO+5(59%) HOMO-8→LUMO(28%)
		280.5	0.0504		HOMO-3→LUMO+1(98%)
		276.8	0.0853		HOMO-8→LUMO(60%)
	4F-TAT	560.8	0.9841		HOMO→LUMO(100%)
		298.5	0.1359		HOMO→LUMO+5(60%) HOMO-7→LUMO(21%)
		280.9	0.1713		HOMO-7→LUMO(71%)
		262.7	0.0638		HOMO-5→LUMO+1(93%)
	4Cl-TAT	595.5	1.2187		HOMO→LUMO(100%)
		344.2	0.0212		HOMO-5→LUMO(85%)
		294.6	0.0111		HOMO-2→LUMO+2(96%)

		294.2	0.2681	HOMO→LUMO+5(+59%)
		279.4	0.0100	HOMO→LUMO+6(79%)
		266.3	0.0815	HOMO-5→LUMO+1(99%)
	4CN-TAT	602.2	1.2911	HOMO→LUMO(100%)
		398.6	0.0121	HOMO→LUMO+2(95%)
		364.0	0.0737	HOMO-5→LUMO(91%)
		313.7	0.0211	HOMO-7→LUMO(85%)
		299.2	0.0110	HOMO-2→LUMO+1(85%)
		284.3	0.0801	HOMO→LUMO+5(37%) HOMO-6→LUMO+1(20%) HOMO-2→LUMO+3(16%) HOMO→LUMO+7(13%)
Emission	TAT	627.1	1.0056	HOMO→LUMO(100%)
		393.0	0.0132	HOMO→LUMO+2(94%)
		296.9	0.0272	HOMO→LUMO+5(49%) HOMO-8→LUMO(45%)
		284.8	0.1808	HOMO-8→LUMO(46%) HOMO→LUMO+5(33%)
		275.1	0.0205	HOMO→LUMO+6(64%) HOMO-7→LUMO(30%)
		251.4	0.0121	HOMO-4→LUMO+2(93%)
	4F-TAT	650.0	0.9720	HOMO→LUMO(100%)
		311.7	0.1149	HOMO→LUMO+5(54%) HOMO-7→LUMO(26%) HOMO-5→LUMO(15%)
		292.0	0.2173	HOMO-7→LUMO(66%) HOMO→LUMO+5(15%) HOMO-5→LUMO(10%)
		282.5	0.0276	HOMO-8→LUMO(63%) HOMO-2→LUMO+2(15%) HOMO→LUMO+6(20%)
		253.3	0.0268	HOMO-5→LUMO+1(97%)
	4Cl-TAT	693.1	1.2079	HOMO→LUMO(100%)
		356.2	0.0159	HOMO-5→LUMO(86%)
		314.8	0.0212	HOMO-8→LUMO(77%) HOMO→LUMO+6(23%)
		304.5	0.2919	HOMO→LUMO+5(62%) HOMO-7→LUMO(18%) HOMO-5→LUMO(11%)
		299.0	0.0191	HOMO→LUMO+6(46%) HOMO-2→LUMO+1(38%) HOMO-8→LUMO(15%)
		292.8	0.0228	HOMO-2→LUMO+1(60%) HOMO→LUMO+6(29%)
	4CN-TAT	710.4	1.2829	HOMO→LUMO(100%)
		409.9	0.0152	HOMO→LUMO+2(93%)

380.5	0.0636	HOMO-5→LUMO(90%)
333.2	0.0280	HOMO-7→LUMO(86%)
324.9	0.0124	HOMO-8→LUMO(87%)
302.3	0.0119	HOMO-2→LUMO+1(63%) HOMO→LUMO+5(33%)

a Measured with UV-vis spectrum technology in chloroform solvent, from ref. 20.

Table S6-1

	TAT		4F-TAT		4Cl-TAT		4CN-TAT	
	hole	electron	hole	electron	hole	electron	hole	electron
λ_{class}(meV)	24	2	40	2	34	0	22	8
S_{eff}	1.944	1.026	1.508	1.354	1.345	1.282	0.973	1.031
ω_{eff}(cm^{-1})	846	1075	1232	974	1197	941	1224	1164

The calculation and selection of relevant parameters in Marcus-Levich-Jortner formulation:

$$k = \frac{2\pi}{\hbar}\frac{\left(V^{eff}\right)^2}{\sqrt{4\pi\lambda_{class}k_BT}}\sum_{n=0}^{\infty}\left[\exp(-S_{eff})\frac{S_{eff}^n}{n!}\times\exp\left(-\frac{(\lambda_{class}+n\hbar\omega_{eff})^2}{4\lambda_{class}k_BT}\right)\right]$$

According to the MLJ equation, we need calculate the three important parameters, including λ_{class}, S_{eff} and ω_{eff} to obtain the CT rate constant *k*. Generally, the λ_{class} should include the outer reorganization energy and the contribution of some low-frequency mode vibrations. For the comparable purposes, we only consider the contribution of low-frequency vibrations (<250cm^{-1}) based on previous studies (Reference 31-32). The S_{eff} term is obtained directly the NM analysis by means of the DUSHIN program. All results are shown in Table S6-2.

Table S6-2

Pathway	Hole transfer		Electron transfer	
	Marcus-Hush model	MLJ model	Marcus-Hush model	MLJ model
1,6,9,14	0.0	0.0	4.057×10^{8}	3.459×10^{8}
2,5,10,13	4.228×10^{7}	3.453×10^{7}	7.152×10^{10}	6.098×10^{10}
3,4,11,12	1.825×10^{10}	2.282×10^{10}	1.491×10^{10}	1.946×10^{10}
7,15	0.0	0.0	2.116×10^{8}	1.804×10^{8}
8,16	1.024×10^{11}	8.366×10^{10}	3.153×10^{13}	2.688×10^{13}

Table S7

Hole transfer		Electron transfer	
approximate relation	random-walk simulation	approximate relation	random-walk simulation
2.290×10^{-5}	1.685×10^{-5}	6.240×10^{-3}	8.799×10^{-4}