Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Delicate Modulation of Triplet Energy Levels for Activating "Hot Excitons" Channel in Deep Red AIEgens

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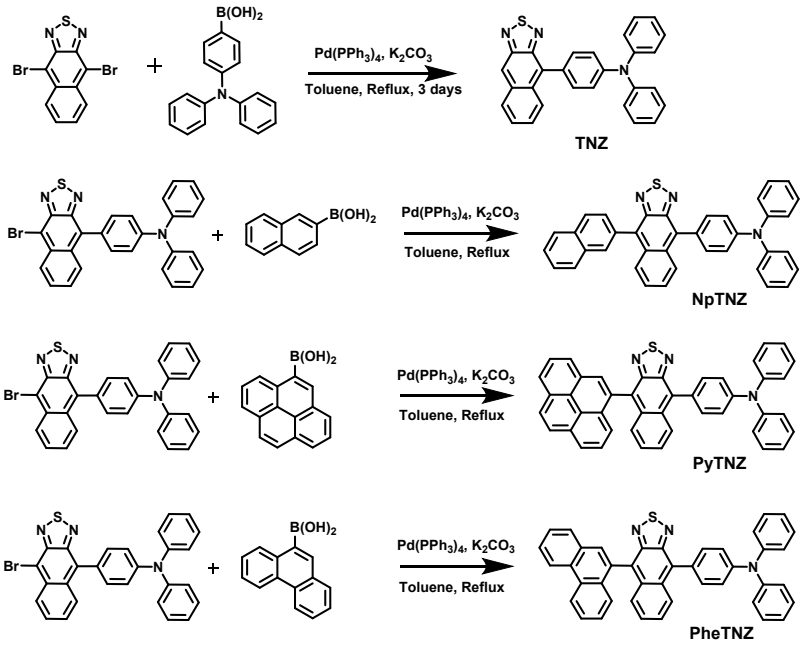

Fig. S1 The synthetic route of TNZ, NpTNZ, PyTNZ and PheTNZ.

Fig. S2 The time of flight mass spectrum of TNZ.

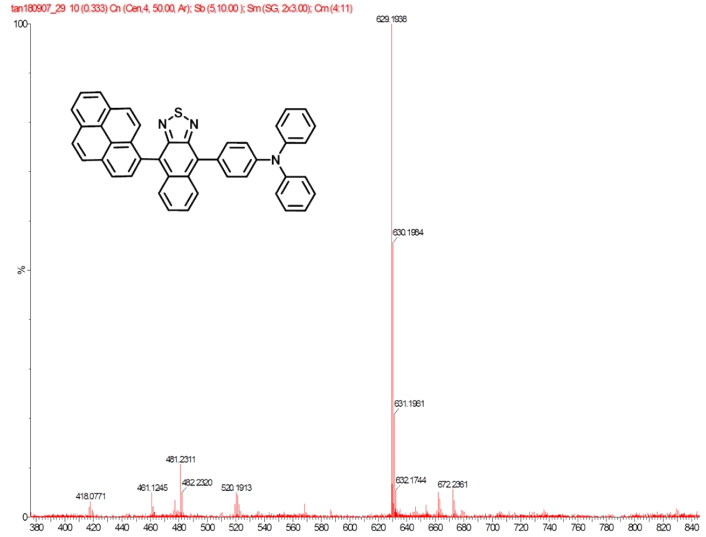

Fig. S3 The time of flight mass spectrum of PyTNZ.

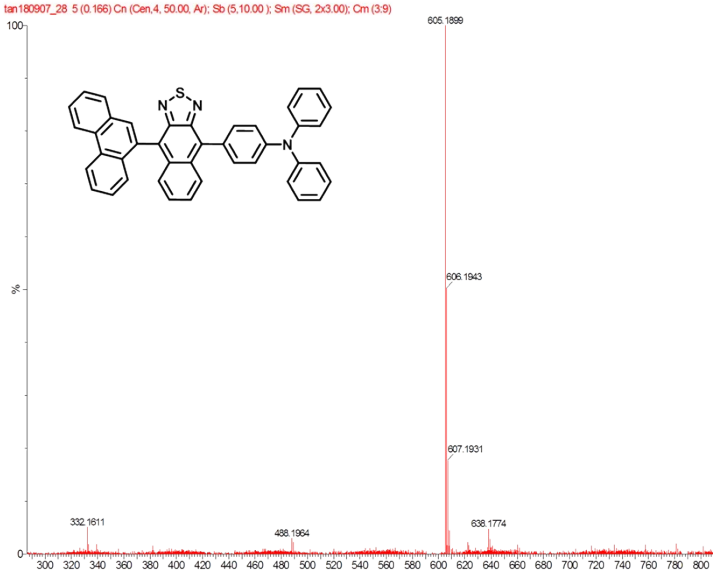

Fig. S4 The time of flight mass spectrum of PheTNZ.

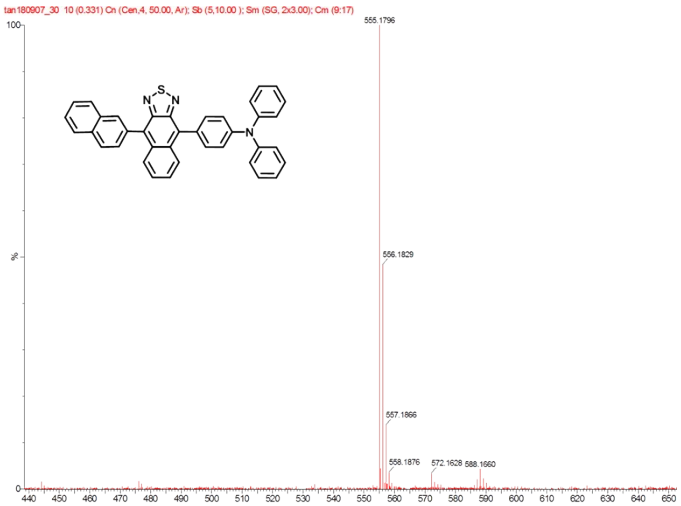

Fig. S5 The time of flight mass spectrum of NpTNZ.

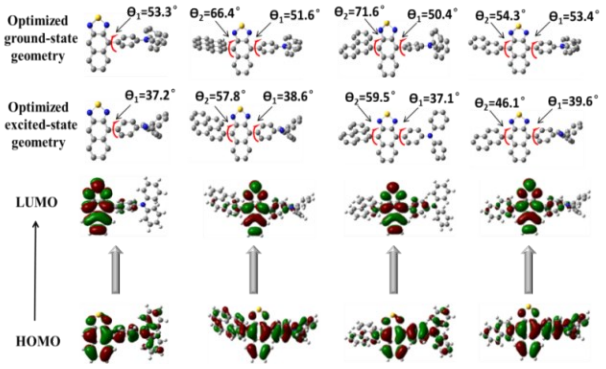

Fig.S6 Calculated optimized ground and excited state geometry and frontier molecular orbital distributions of TNZ, PyTNZ, PheTNZ and NpTNZ under absorption transition process.

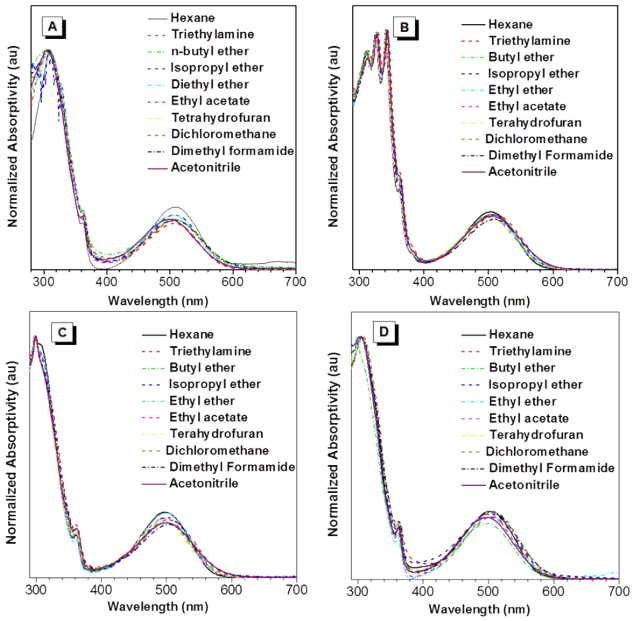

Fig. S7 UV-vis absorption spectra of chromophores in various organic solvents with different polarity: (A) TNZ, (B) PyTNZ, (C) PheTNZ and (D) NpTNZ.

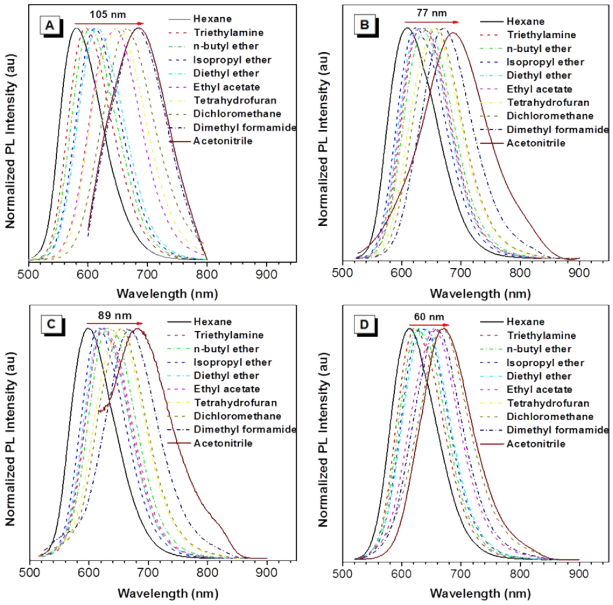

Fig. S8 PL emission spectra of chromophores in various organic solvents with different polarity: (A) TNZ, (B) PyTNZ, (C) PheTNZ and (D) NpTNZ.

Table S1 Photophysical data of TNZ in different solvents.

Solvents	Δf	λ_{abs} [a]	λ_{em} [b]	Stokes shift	Φ_F [c]	Lifetime [d]
		[nm]	[nm]	[cm^{-1}]	[%]	[ns]
Hexane	0	485	578	3317	77.5	13.85
Triethylamine	0.048	488	597	3741	51.1	12.85
Butyl ether	0.096	488	605	3963	80.2	13.21
Isopropyl ether	0.145	488	610	4098	80.9	15.26
Ethyl ether	0.167	480	614	4546	89.6	15.69
Ethyl Acetate	0.2	489	651	5089	61.8	11.48
Tetrahydrofuran	0.21	487	650	5149	57.5	11.38
Dichloromethane	0.217	494	665	5205	28.6	7.64
Dimethyl Formamide	0.276	488	685	5893	1.1	2.1
Acetonitrile	0.305	479	681	6192	2.3	1.7

[a] Absorption peak; [b] Emission peak; [c] Fluorescence quantum yield; [d] fluorescence lifetime.

Table S2 Photophysical data of PyTNZ in different solvents.

Solvents	Δf	λ_{abs} [a]	λ_{em} [b]	Stokes shift	Φ_F [c]	Lifetime [d]
		[nm]	[nm]	[cm^{-1}]	[%]	[ns]
Hexane	0	503	609	3460	57.0	8.45
Triethylamine	0.048	510	633	3810	68.5	9.68
Butyl ether	0.096	505	624	3776	69.3	10.09
Isopropyl ether	0.145	503	628	3957	69.8	10.21
Ethyl ether	0.167	501	635	4212	67.4	11.26
Ethyl Acetate	0.2	501	654	4669	56.1	10.77
Tetrahydrofuran	0.21	506	658	4565	53.9	9.40
Dichloromethane	0.217	508	670	4760	41.2	8.56
Dimethyl Formamide	0.276	506	686	5186	2.3	10.51
Acetonitrile	0.305	497	678	5371	1.0	2.68

[a] Absorption peak; [b] Emission peak; [c] Fluorescence quantum yield; [d] fluorescence lifetime.

Table S3 Photophysical data of PheTNZ in different solvents.

Solvents	Δf	λ_{abs} [a]	λ_{em} [b]	Stokes shift	Φ_F [c]	Lifetime [d]
		[nm]	[nm]	[cm^{-1}]	[%]	[ns]
Hexane	0	495	598	3480	87.4	12.78
Triethylamine	0.048	502	624	3895	82.2	12.29
Butyl ether	0.096	500	616	3766	83.2	12.71
Isopropyl ether	0.145	500	623	3948	79.7	12.91
Ethyl ether	0.167	496	626	4187	80.1	13.39
Ethyl Acetate	0.2	493	649	4876	55.7	10.97
Tetrahydrofuran	0.21	497	653	4807	51.9	10.02
Dichloromethane	0.217	504	667	4849	37.1	8.72
Dimethyl Formamide	0.276	497	687	5564	2.2	1.57

Acetonitrile	0.305	494	681	5558	1.2	1.28

[a)] Absorption peak; [b)] Emission peak; [c)] Fluorescence quantum yield; [d)] fluorescence lifetime.

Table S4 Photophysical data of NpTNZ in different solvents.

Solvents	Δf	λ_{abs} [a)] [nm]	λ_{em} [b)] [nm]	Stokes shift [cm^{-1}]	Φ_F [c)] [%]	Lifetime [d)] [ns]
Hexane	0	503	611	3514	80.7	11.98
Triethylamine	0.048	505	624	3766	76.2	11.05
Butyl ether	0.096	503	627	3932	72.6	11.38
Isopropyl ether	0.145	501	639	4311	72.9	11.09
Ethyl ether	0.167	503	643	4329	70.8	11.32
Ethyl Acetate	0.2	502	656	4676	53.8	9.47
Tetrahydrofuran	0.21	505	659	4627	52.3	8.66
Dichloromethane	0.217	506	668	4793	45.3	8.70
Dimethyl Formamide	0.276	504	671	4938	3.5	9.34
Acetonitrile	0.305	499	671	5137	3.3	8.92

[a)] Absorption peak; [b)] Emission peak; [c)] Fluorescence quantum yield; [d)] fluorescence lifetime.

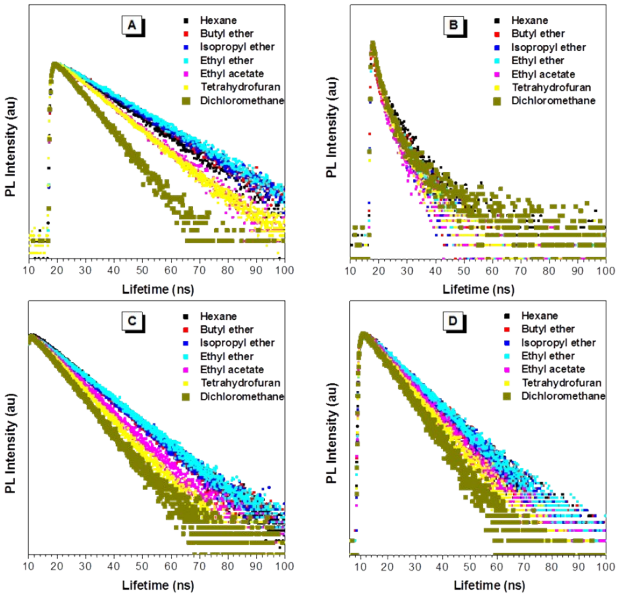

Fig. S9 Transient photoluminescence decay spectra in different solvent media: (A) TNZ, (B) PyTNZ, (C) PheTNZ, (D) NpTNZ.

Table S5 Theoretical emission peaks vs experimental values for TNZ-based emitters.

	Experimental result (nm)	Theoretical simulation (nm)		
Sample	Hexane	M06-2X	B3LYP	PBE1PBE
TNZ	577	578	618	684
PyTNZ	623	609	772	719
PheTNZ	620	598	784	704
NpTNZ	622	611	772	709

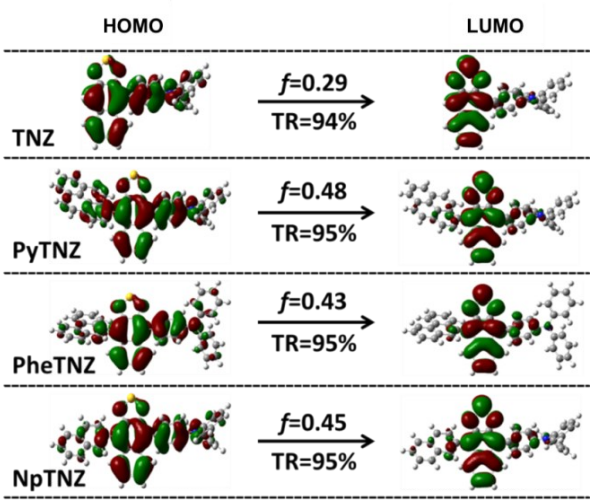

Fig. S10 The emission decay based on the optimized S_1 configuration (*f* and TR represents oscillator strength and transition ratio).

Table S6 Theoretical simulation of singlet and triplet energy levels.

Compound	S_1 eV	S_2 eV	T_1 eV	T_2 eV	T_3 eV	T_4 eV	ΔT_2T_1 (eV)
Py	3.83	3.95	2.39	3.63	3.68	3.98	1.24
Phe	4.07	4.45	2.99	3.71	3.77	3.93	0.72
Np	4.50	4.64	3.00	4.11	4.23	4.66	1.11
TNZ	2.15	3.10	0.77	2.61	2.96	3.16	1.84
PyTNZ	1.99	2.81	0.72	2.40	2.58	2.86	1.68
PheTNZ	2.00	3.03	0.69	2.61	2.89	3.03	1.92
NpTNZ	1.99	2.98	0.68	2.59	2.96	3.01	1.91

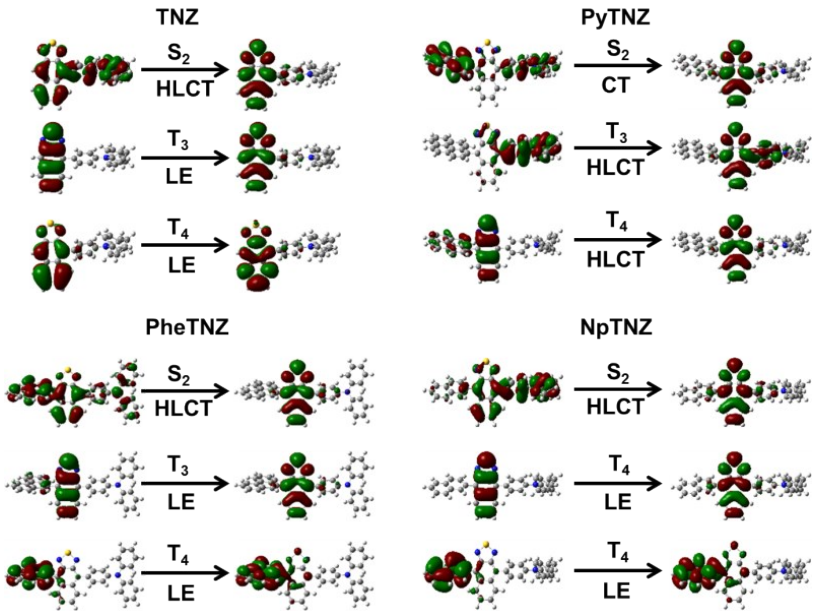

Fig. S11 Electrons distribution on the S_2, T_3, T_4 platforms for these DR emitters.

Table S7 Calculated energy gap between pure LE and pure CT states based on ground state.

E (eV)	TNZ	PyTNZ	PheTNZ	NpTNZ
E_{LE}	3.14	3.14	3.14	3.14
E_{S1}	2.77	2.64	2.65	2.65
E_{S2}	3.37	3.17	3.33	3.27
E_{CT}	3.00	2.67	2.84	2.78
δE	0.60	0.53	0.68	0.62
ΔE	0.07	0.24	0.15	0.18
J	0.29	0.11	0.31	0.25

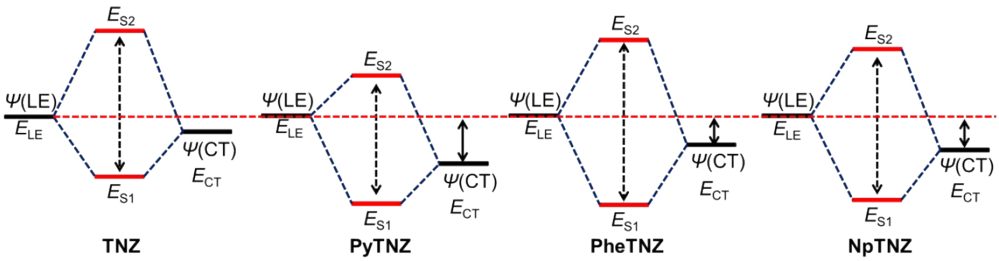

Fig. S12 Schematic diagram of hybridization process of LE and CT states for four NZ-based emitters.

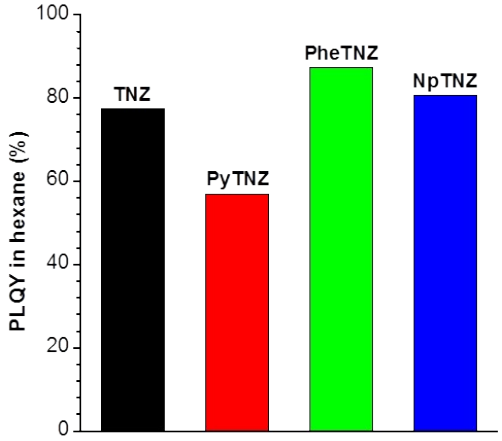

Fig. S13 PLQYs of four emitters in low-polarity hexane.

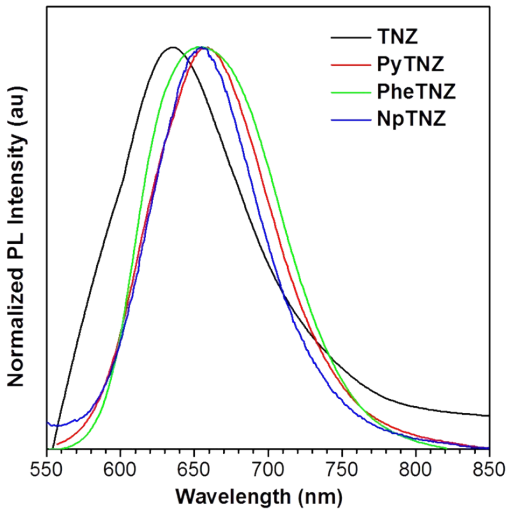

Fig. S14 PL spectra of TNZ, PyTNZ, PheTNZ and NpTNZ in the film.

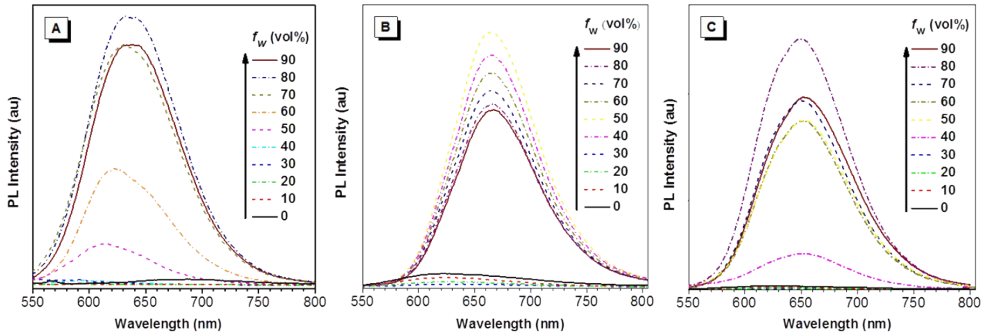

Fig. S15 PL spectra of (A) TNZ, (B) PyTNZ , (C) PheTNZ in DMF/water mixtures with different water fractions.

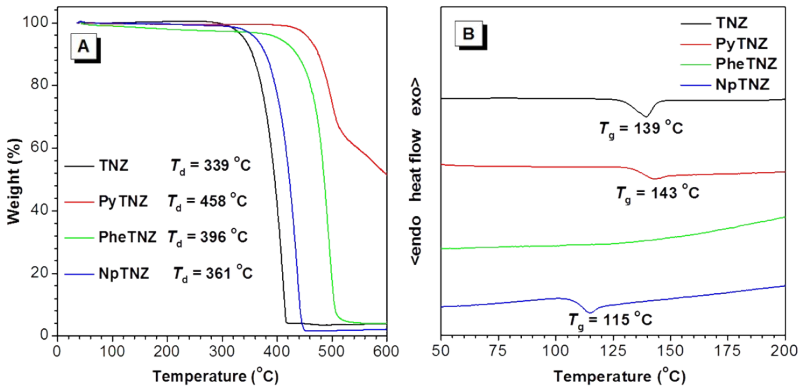

Fig. S16 Thermodynamic properties: (A) The TGA and (B) DSC curves.

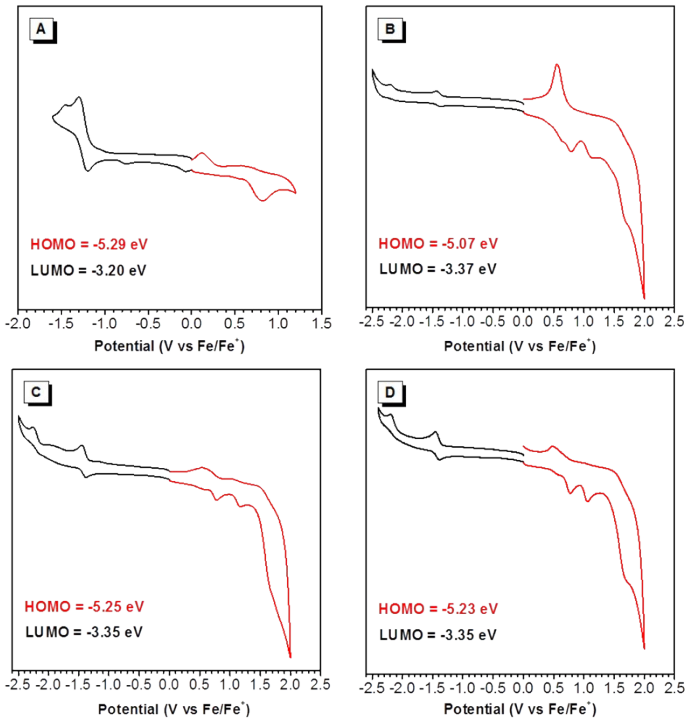

Fig. S17 Cyclic voltammograms (CV) of these investigated compounds: (A) TNZ, (B) PyTNZ, (C) PheTNZ, (D) NpTNZ.