Electronic supporting information

Theoretical study and design of AIE-type TADF materials derivating from spatially conjugated [2.2]paracyclophane

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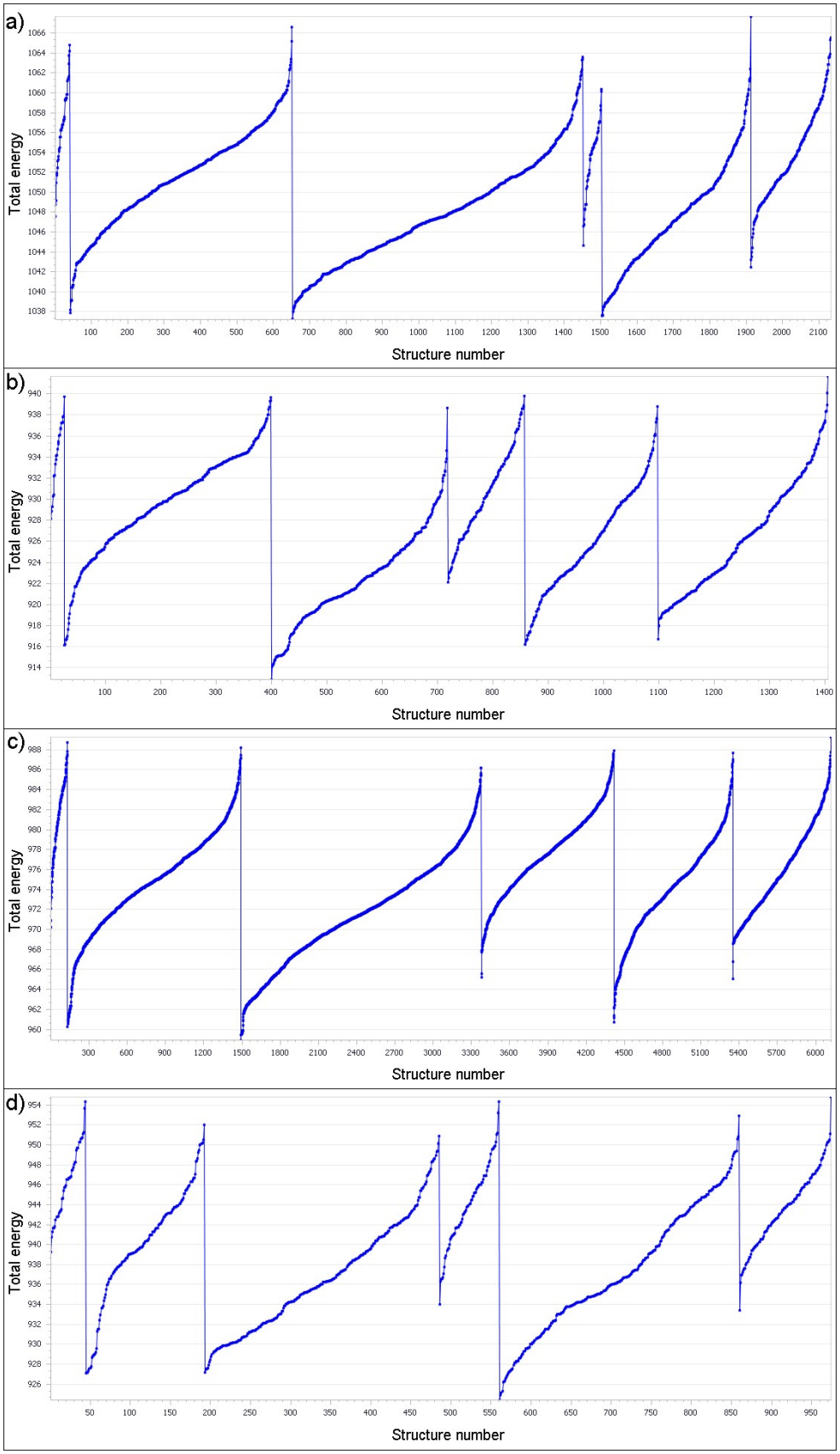

Fig. S1. The molecular interaction energies (a.u.) in different crystal packing structures predicted under the C2/C, P-1, P21, P21/C, P212121 and PBCA space groups (from left to right) for molecules **1-4** (a-d).

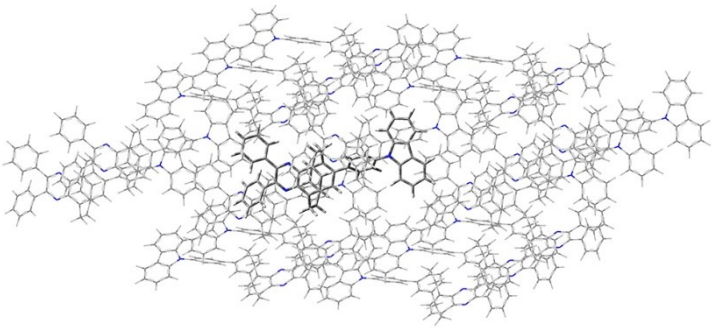

Fig. S2. A QM/MM model based on the simulated stacking structure of molecule **1** with the central molecule as the QM region.

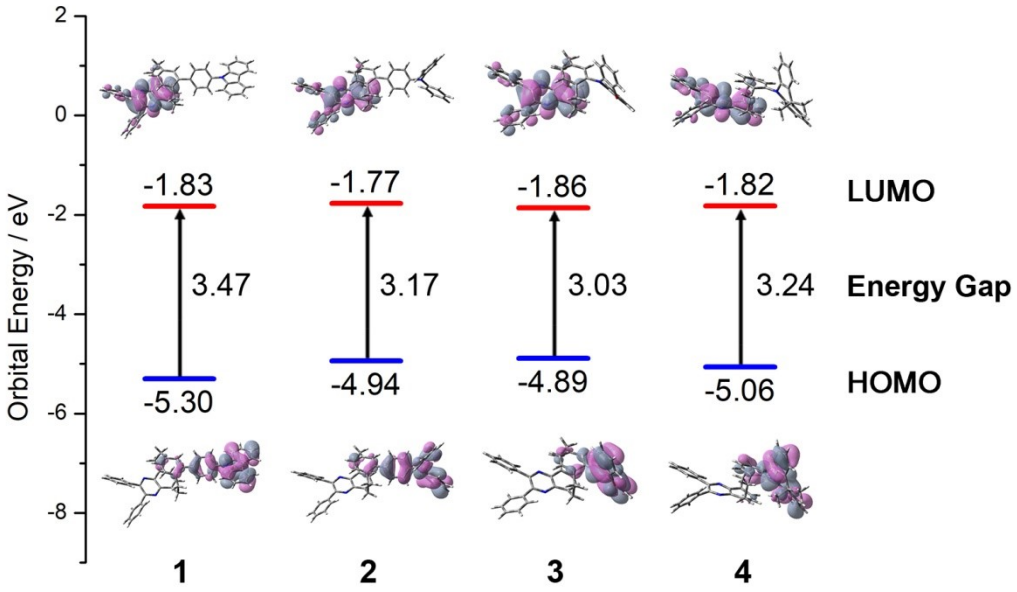

Fig. S3. Frontier molecular orbital diagrams and the respective energy levels and energy gaps of **1-4** in aggregate state at the S_0 geometry.

Table S1 The transition densities of TSCT and TBCT for molecules **1-4** in isolated (a) and aggregated (b) states calculated by the IFCT method.

	transition densities			
	isolated molecule		monomer in crystal	
	TSCT	TBCT	TSCT	TBCT
1	78.4%	2.1%	92.3%	2.7%
2	96.8%	1.8%	95.4%	2.4%
3	96.4%	1.8%	95.6%	2.4%
4	96.0%	1.9%	94.4%	2.7%

Table S2 Calculated singlet and triplet excitation energies (eV) at the optimized S_0 geometries for isolated **1-4**.

	1		**2**		**3**		**4**	
n	S_n	T_n	S_n	T_n	S_n	T_n	S_n	T_n
1	3.1495	2.5585	2.7740	2.5532	2.5149	2.4879	2.7212	2.5393
2	3.4243	2.8902	3.3716	2.7426	3.1086	2.5543	3.3191	2.6935
3	3.4746	3.1021	3.4072	2.9417	3.4418	2.9342	3.4342	2.9494
4	3.5878	3.1736	3.4598	3.0601	3.5123	3.0028	3.5192	3.0984
5	3.6804	3.2842	3.5806	3.1049	3.5559	3.0994	3.5943	3.2061
6	3.6913	3.4006	3.6870	3.3509	3.5988	3.2049	3.7097	3.4110
7	3.7323	3.4093	3.7802	3.3668	3.7183	3.2887	3.7970	3.4641
8	3.9500	3.4528	3.9041	3.4535	3.7989	3.4070	4.0445	3.5771
9	3.9916	3.5387	3.9497	3.4963	3.9895	3.5651	4.1066	3.5986
10	4.0439	3.5794	4.0231	3.5133	4.0091	3.5894	4.1499	3.6235
11		3.6788		3.5670		3.6206		3.7077
12		3.6804		3.5949		3.6520		3.8436
13		3.7331		3.7280		3.7623		3.8677
14		3.8118		3.9024		3.8251		3.9251
15		3.9038		3.9398		3.8867		3.9633
16		3.9734		3.9608		3.9547		4.0230
17		4.0291		4.0104		3.9880		4.0325
18		4.0376		4.0216		4.0200		4.0868
19		4.0580		4.0483		4.0294		4.1194
20		4.0881		4.0867		4.0609		4.1298

Table S3 Energy differences [$\Delta E(S_n\text{-}T_1)$/eV] between the singlet states with relatively large oscillator strength and their neighboring triplets states (T_n) and the corresponding SOC matrix elements ($\langle S|\boldsymbol{H}_{SOC}|T_n\rangle$/cm^{-1}) and ISC rate ($k_{ISC}$/s^{-1}) for isolated **1-4**.

1							
T_n	$\Delta E(S_2\text{-}T_n)$	$\langle S_2\|\boldsymbol{H}_{SOC}\|T_n\rangle$	k_{ISC}	T_n	$\Delta E(S_3\text{-}T_n)$	$\langle S_3\|\boldsymbol{H}_{SOC}\|T_n\rangle$	k_{ISC}
T_3	0.3222	0.44	1.54×10^{7}	T_4	0.3010	**1.60**	$\mathbf{1.95\times10^{8}}$
T_4	0.2507	**2.13**	$\mathbf{3.05\times10^{8}}$	T_5	0.1904	**0.97**	$\mathbf{5.12\times10^{7}}$
T_5	0.1401	**0.74**	$\mathbf{2.33\times10^{7}}$	T_6	0.0740	**0.75**	$\mathbf{1.52\times10^{7}}$
T_6	0.0237	0.28	1.30×10^{6}	T_7	0.0653	0.08	1.61×10^{5}
T_7	0.0150	0.16	3.83×10^{5}	T_8	0.0218	**0.61**	$\mathbf{6.04\times10^{6}}$
T_8	-0.0285	0.42	1.89×10^{6}	T_9	-0.0641	0.01	1.74×10^{3}
T_9	-0.1144	0.02	1.09×10^{4}	T_{10}	-0.1048	**1.24**	$\mathbf{3.91}\times10^{7}$
2							
T_n	$\Delta E(S_2\text{-}T_n)$	$\langle S_2\|\boldsymbol{H}_{SOC}\|T_n\rangle$	k_{ISC}	T_n	$\Delta E(S_4\text{-}T_n)$	$\langle S_4\|\boldsymbol{H}_{SOC}\|T_n\rangle$	k_{ISC}
T_4	0.3115	**4.80**	$\mathbf{4.75\times10^{9}}$	T_6	0.1089	0.42	3.52×10^{7}
T_5	0.2667	0.48	4.70×10^{7}	T_7	0.0930	0.02	4.46×10^{4}
T_6	0.0207	**0.92**	$\mathbf{2.91\times10^{7}}$	T_8	0.0063	**0.72**	$\mathbf{1.21\times10^{7}}$
T_7	0.0048	0.02	8.98×10^{3}	T_9	-0.0365	**0.76**	$\mathbf{8.93\times10^{7}}$
T_8	-0.0819	**1.06**	$\mathbf{2.08\times10^{8}}$	T_{10}	-0.0535	**0.62**	$\mathbf{6.43\times10^{7}}$
				T_{11}	-0.1072	0.09	1.61×10^{6}
3							
T_n	$\Delta E(S_3\text{-}T_n)$	$\langle S_3\|\boldsymbol{H}_{SOC}\|T_n\rangle$	k_{ISC}	T_n	$\Delta E(S_4\text{-}T_n)$	$\langle S_4\|\boldsymbol{H}_{SOC}\|T_n\rangle$	k_{ISC}
T_5	0.3424	0.13	7.16×10^{5}	T_6	0.3074	0.48	9.75×10^{6}
T_6	0.2369	0.26	2.85×10^{6}	T_7	0.2236	**0.94**	$\mathbf{3.72\times10^{7}}$
T_7	0.1531	**1.30**	$\mathbf{7.07\times10^{7}}$	T_8	0.1053	0.18	1.35×10^{6}
T_8	0.0348	0.24	2.37×10^{6}	T_9	-0.0528	**0.66**	$\mathbf{1.87\times10^{7}}$

T_9	-0.1233	**0.90**	**3.49×10^7**	T_{10}	-0.0771	**0.91**	**3.56×10^7**
				T_{11}	-0.1083	**0.73**	**2.29×10^7**

4

T_n	$\Delta E(S_4\text{-}T_n)$	$\langle S_4\|\boldsymbol{H}_{SOC}\|T_n\rangle$	k_{ISC}
T_5	0.3131	0.17	6.61×10^6
T_6	0.1082	**0.79**	**1.87×10^8**
T_7	0.0551	0.19	8.47×10^6
T_8	-0.0579	**1.15**	**3.64×10^8**
T_9	-0.0794	0.38	4.09×10^7
T_{10}	-0.1043	0.11	3.44×10^6