Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Host-guest interaction induced room-temperature phosphorescence enhancement of organic dyes: a computational study

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I. Supplementary Figures

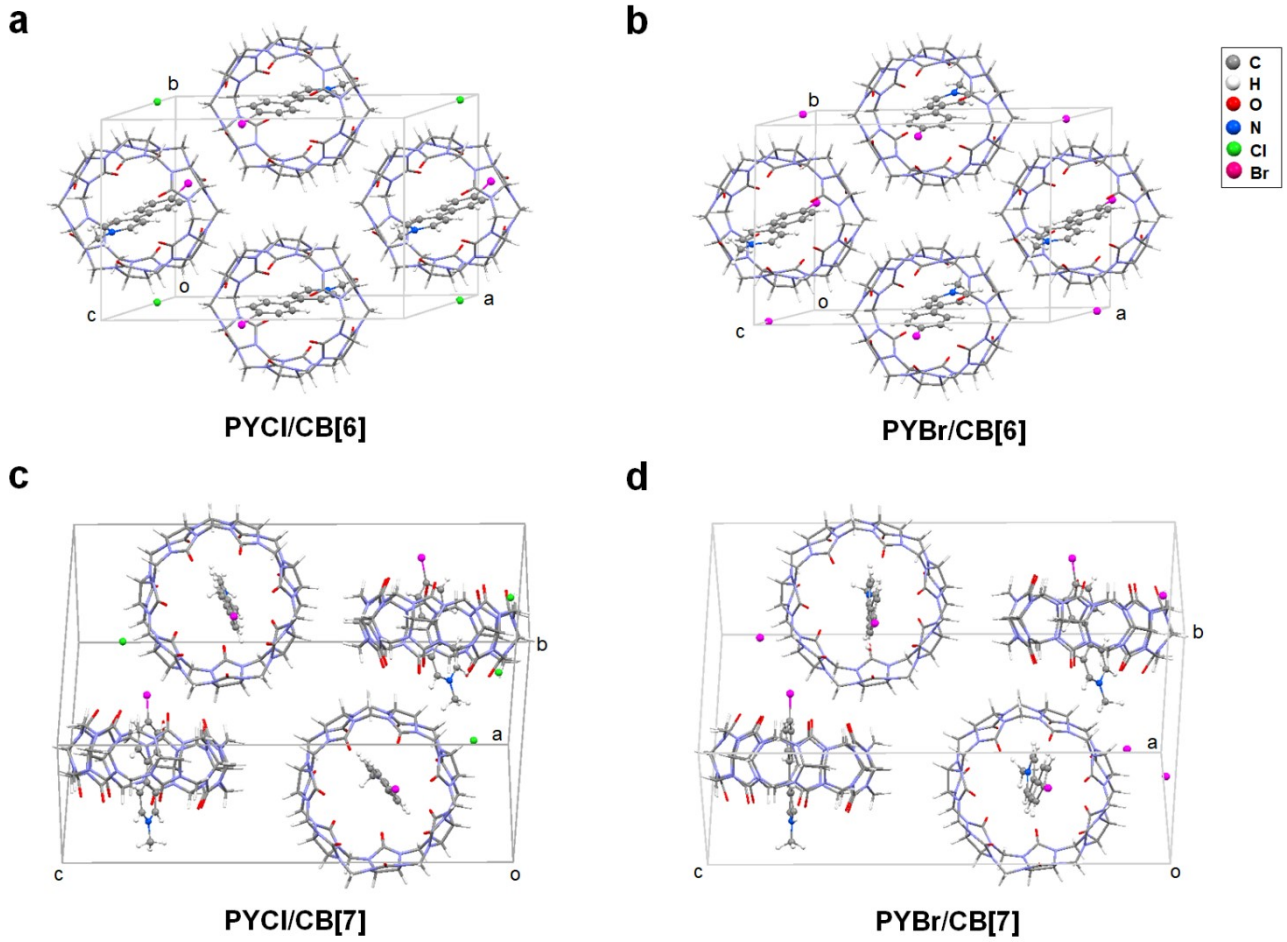


Fig. S1 The optimized unit cell structure of four host-guest complexes: (a) PYCl/CB[6], (b) PYBr/CB[6], (c) PYCl/CB[7], (d) PYBr/CB[7].

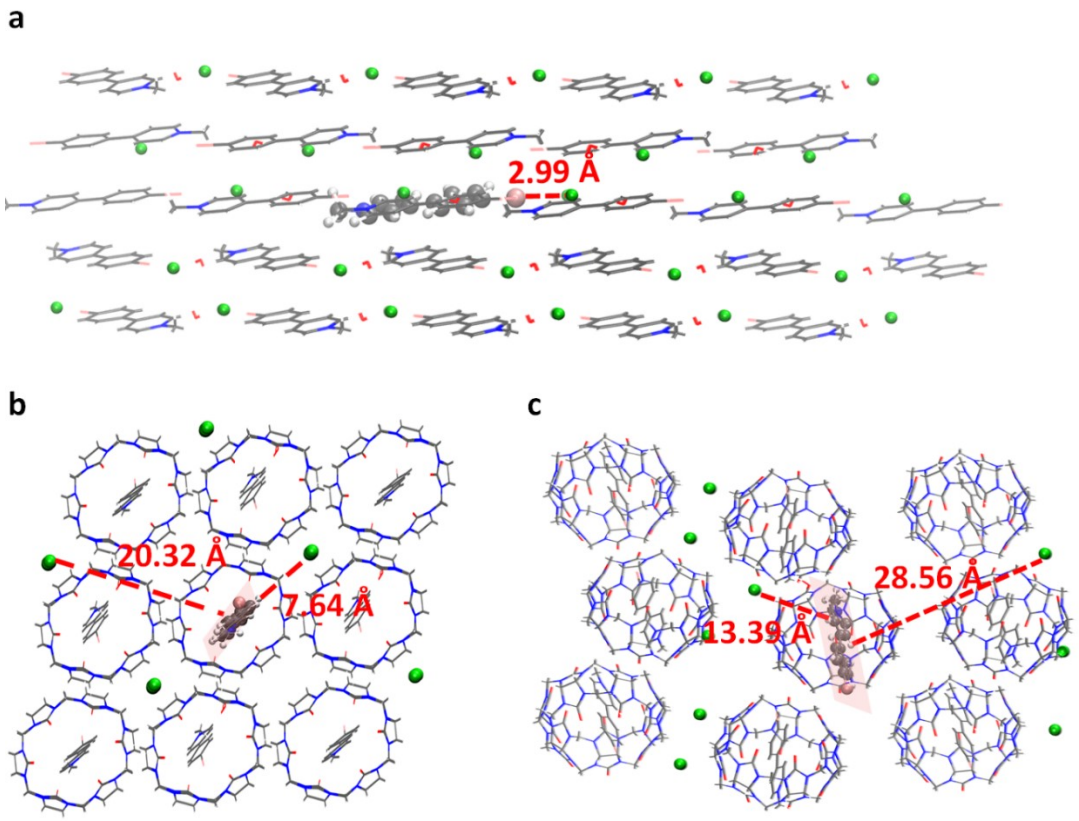


Fig. S2 The QM/MM model of (a) PYCl, (b) PYCl/CB[6] and (c) PYCl/CB[7] with the representative distance between the plane of PY^+ and the counterion labeled.

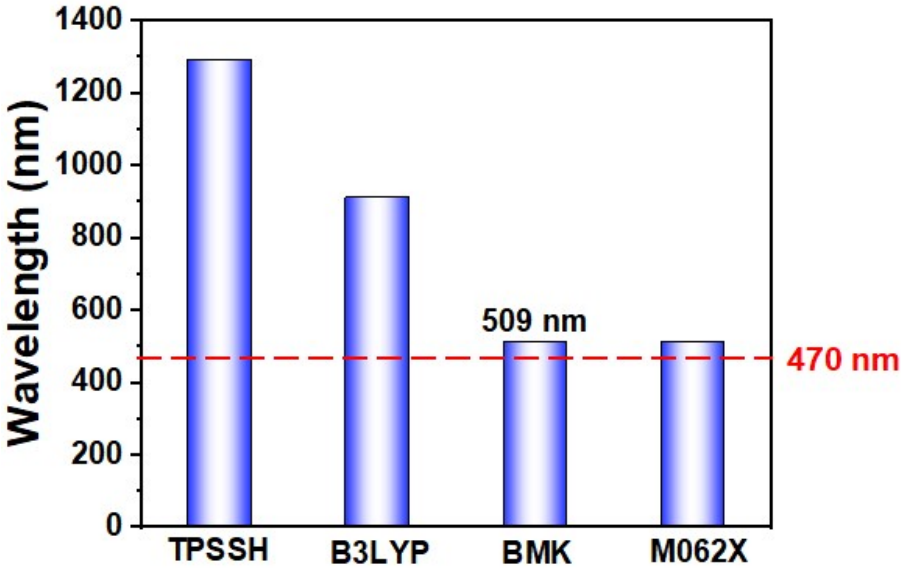


Fig. S3 The wavelength of Phosphorescence at T_1-geometry calculated by different functionals, including TPSSH, B3LYP, BMK and M06-2X coupled with 6-31G** basis set for PYBr.

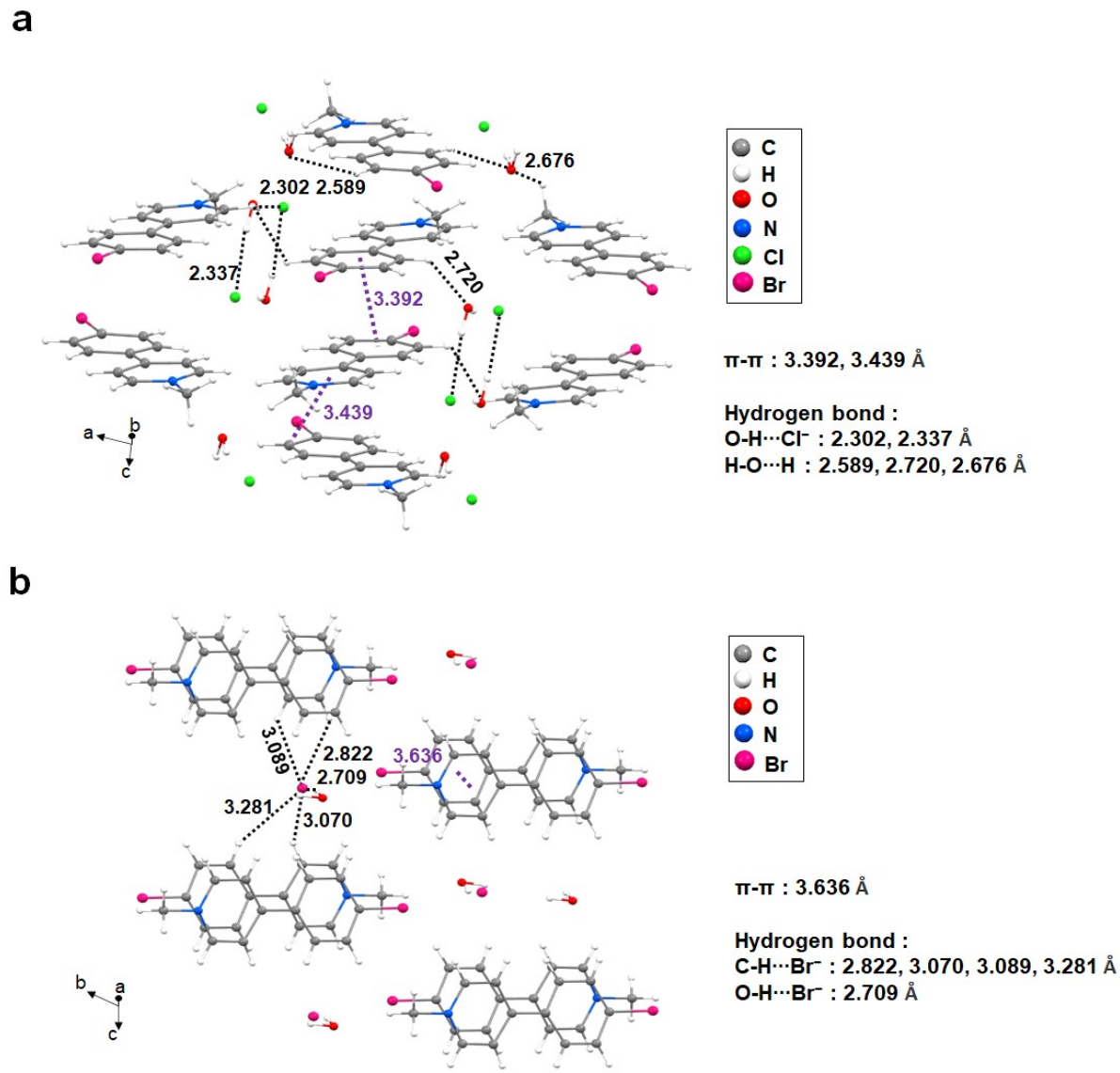


Fig. S4 Single-crystal X-ray diffraction analysis of (a) PYCl, (b) PYBr. The dotted line shows the π-π interaction force between two adjacent molecules and hydrogen bond. Here, H-bond with the distance between the donor (D) and acceptor (A) atoms is less than 3.5 Å, and the angle of D-H-A is greater than 135°.

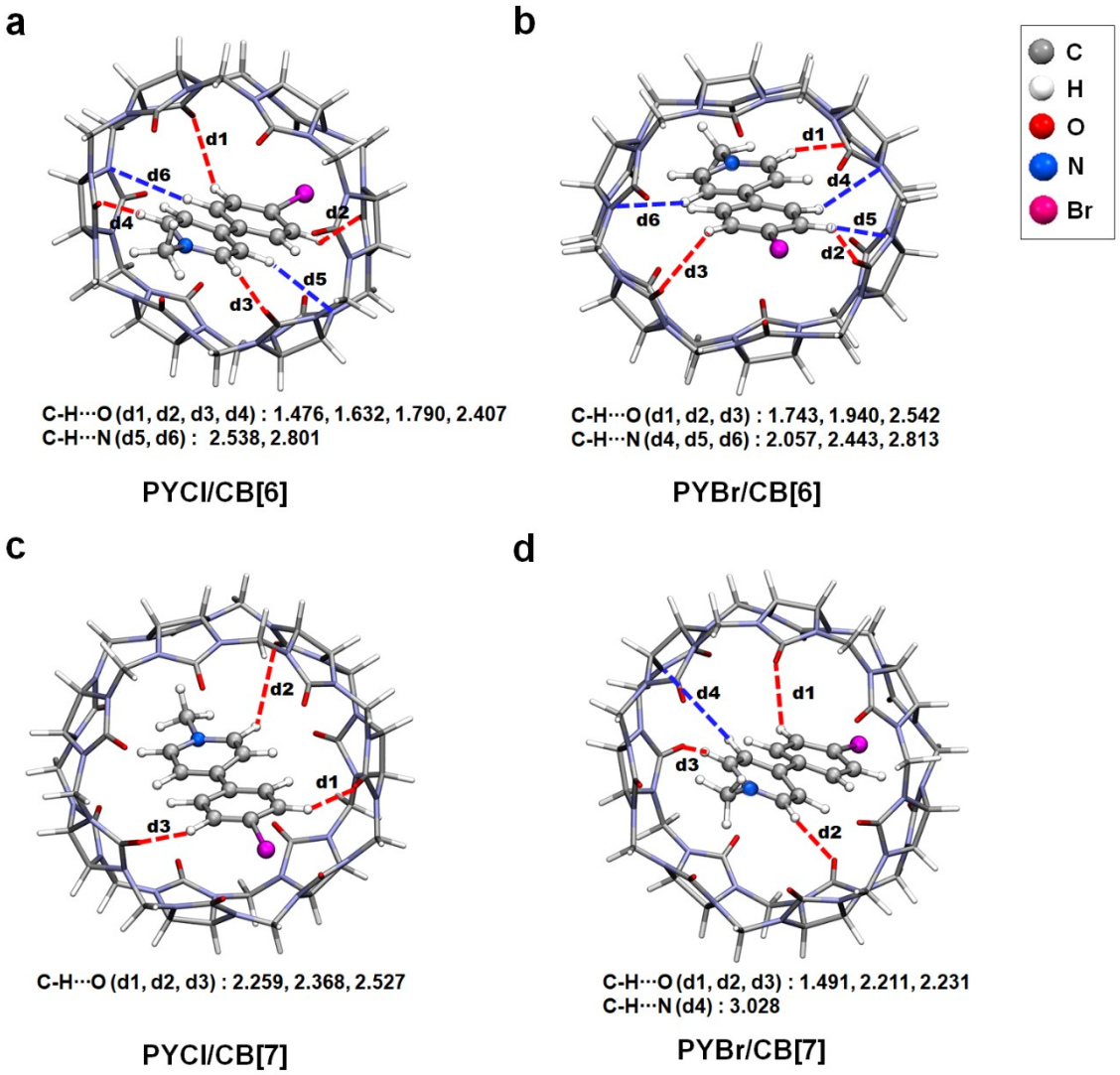


Fig. S5 Intermolecular interactions of (a) PYCl/CB[6], (b) PYBr/CB[6], (c) PYCl/CB[7], (d) PYBr/CB[7].

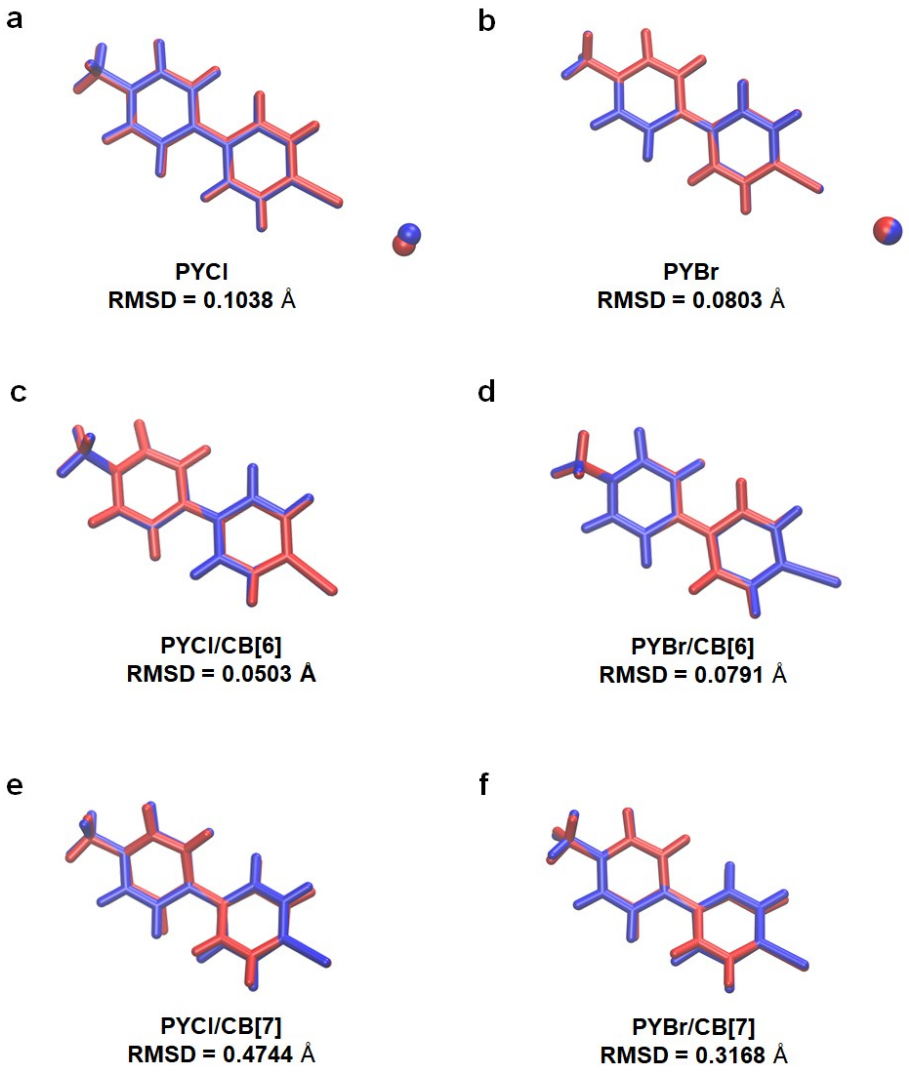


Fig. S6 The structural superposition and RMSD values of (a) PYCl, (b) PYBr, (c) PYCl/CB[6], (d) PYBr/CB[6], (e) PYCl/CB[7], (f) PYBr/CB[7] in the optimized S_0 and T_1 geometries in crystals.

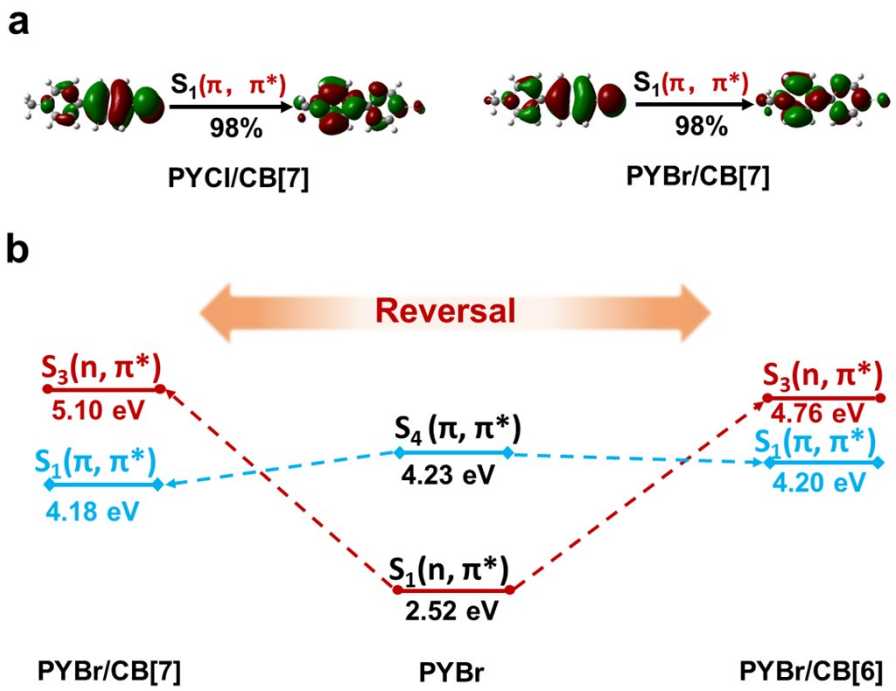


Fig. S7 (a) The frontier molecular orbitals at S_1-geometry of (a) PYCl/CB[7], PYBr/CB[7]. (b) The energy levels of key transition orbitals and the corresponding transition properties of the PYBr, PYBr/CB[6] and PYBr/CB[7] at S_1.

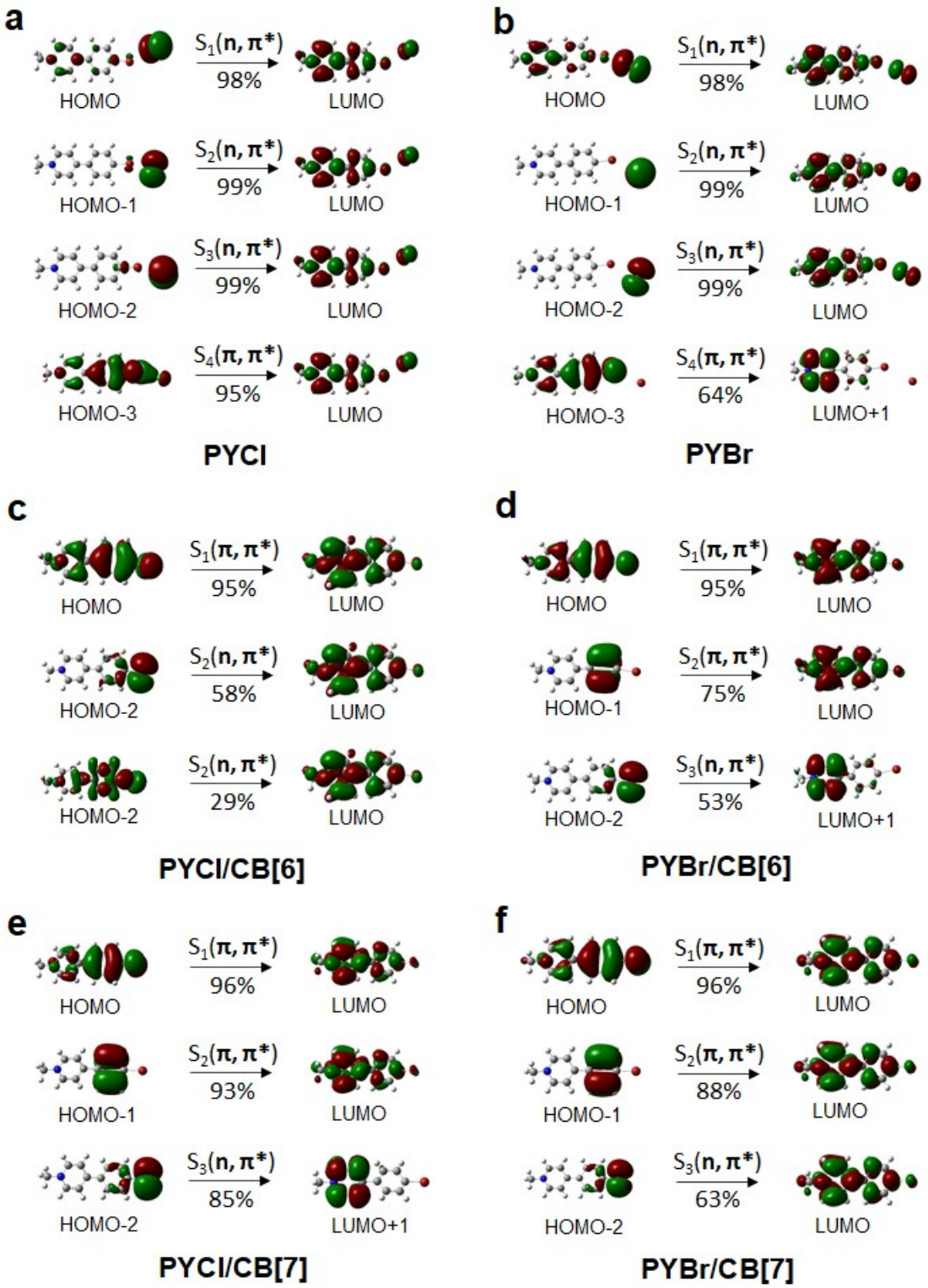


Fig. S8 The transition orbitals for the excited singlet state S_n ($n \leq 4$) of (a) PYCl, (b) PYBr, (c) PYCl/CB[6], (d) PYBr/CB[6], (e) PYCl/CB[7], (f) PYBr/CB[7].

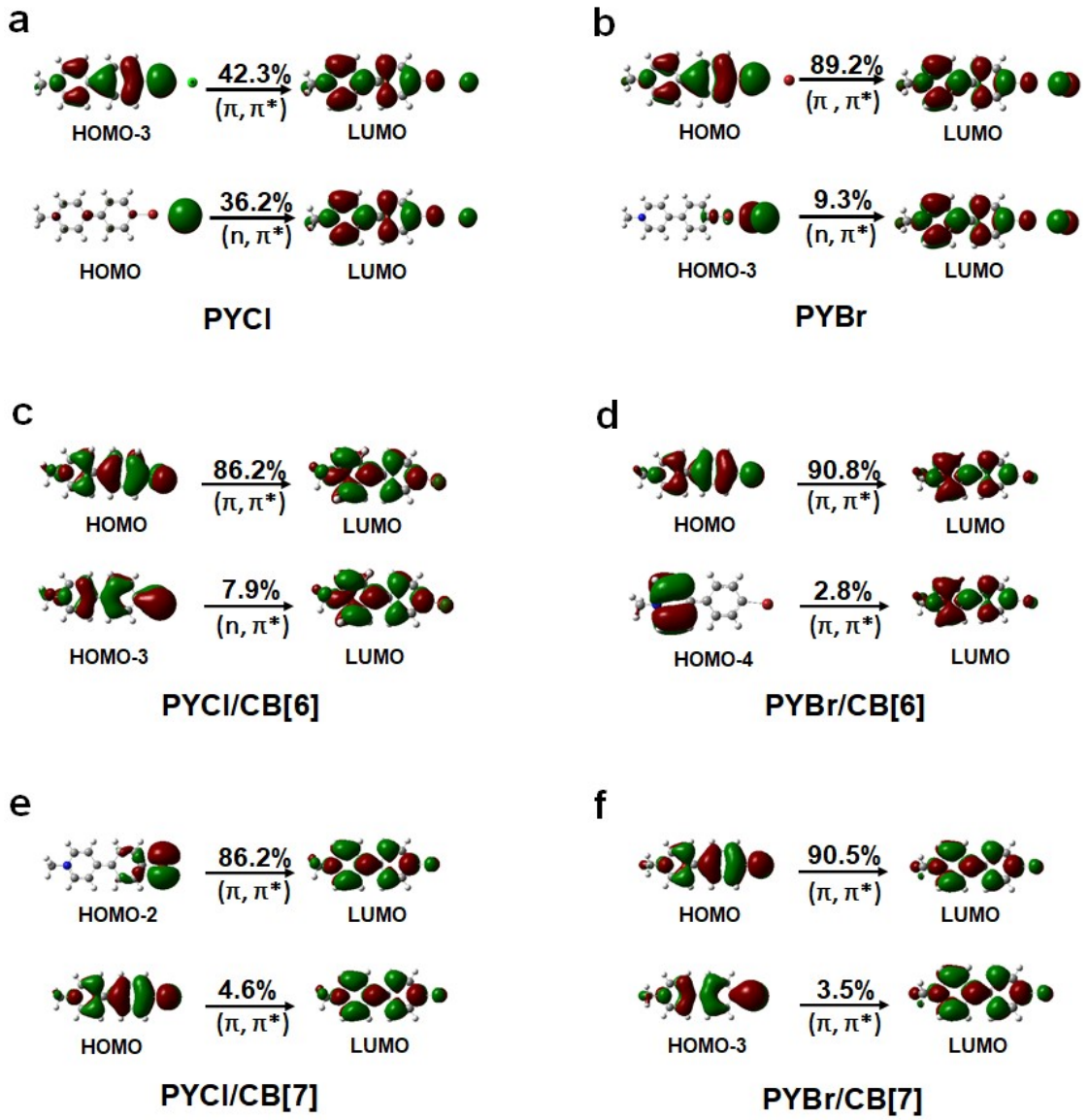


Fig. S9 The frontier natural molecule transition orbitals for the T_1 of (a) PYCl, (b) PYBr, (c) PYCl/CB[6], (d) PYBr/CB[6], (e) PYCl/CB[7], (f) PYBr/CB[7].

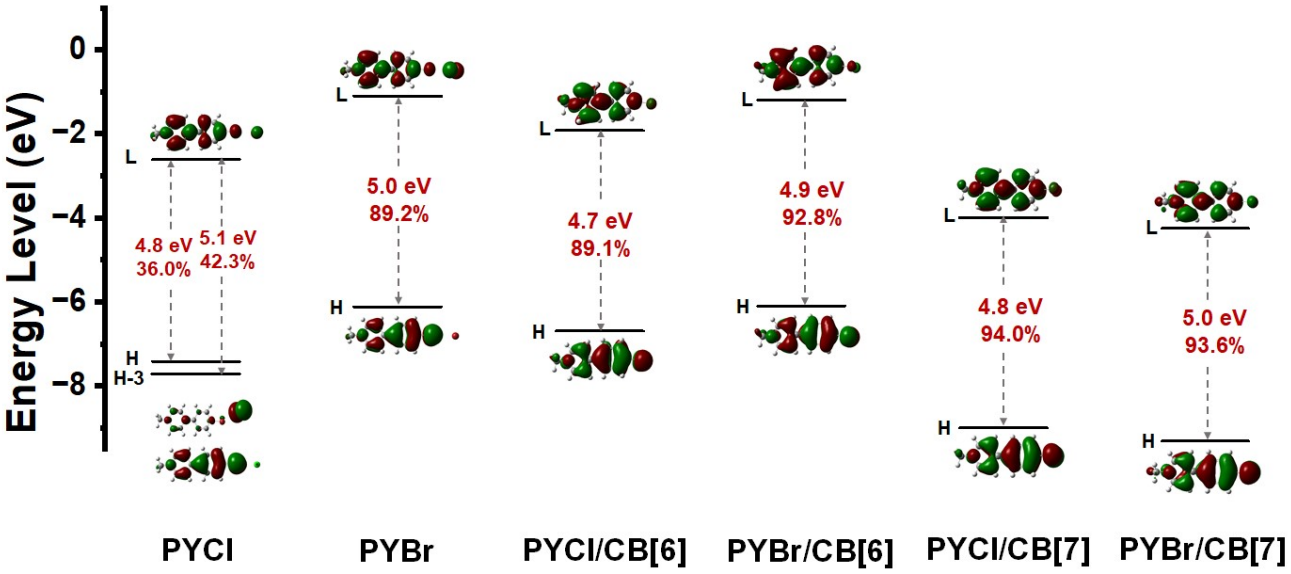


Fig. S10 Energy level of HOMO, LUMO, and the corresponding energy gap based on T_1 geometries of the studied molecules. "H" means the "HOMO", "L" means the "LUMO".

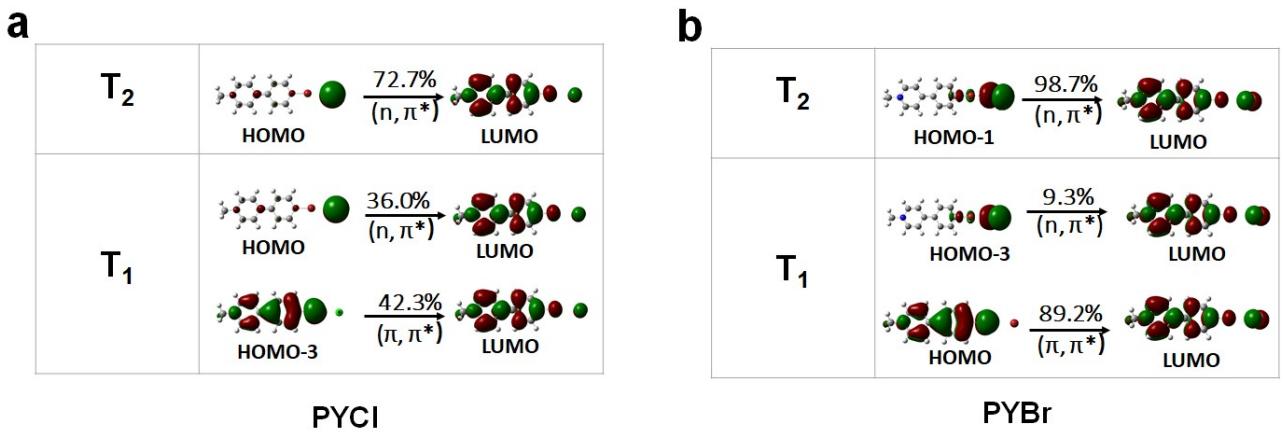


Fig. S11 Transition orbitals of the high-lying triplet states of (a) PYCl and (b) PYBr.

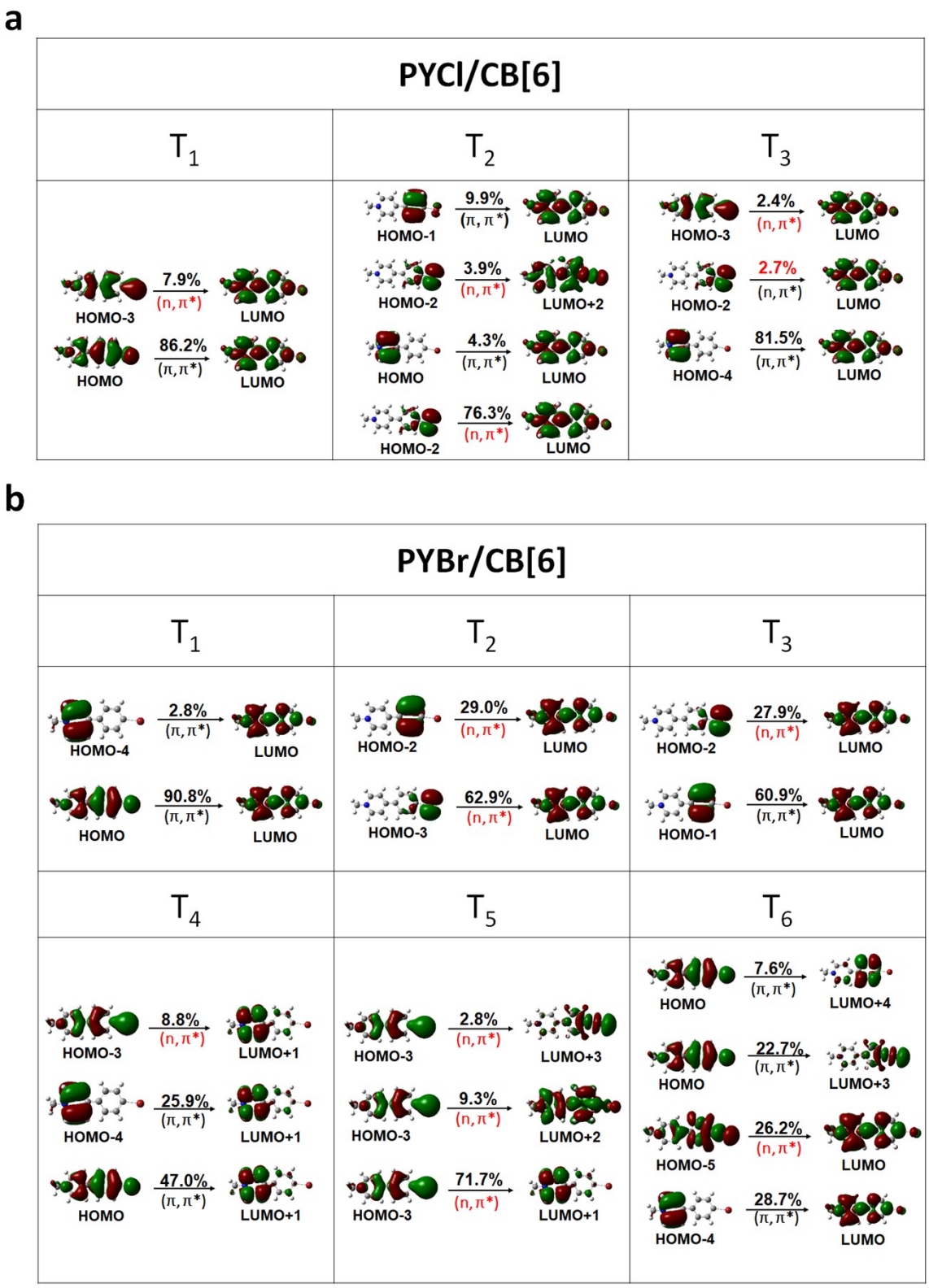
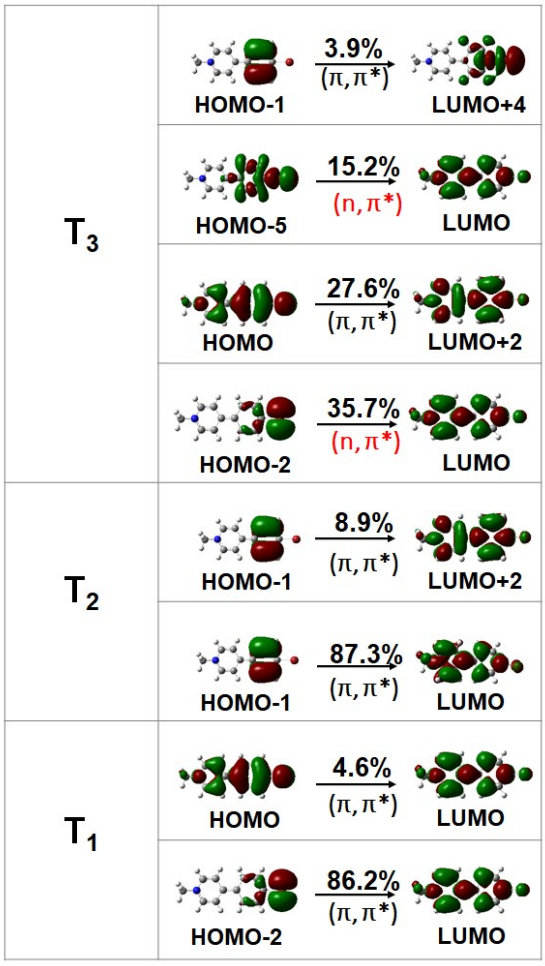
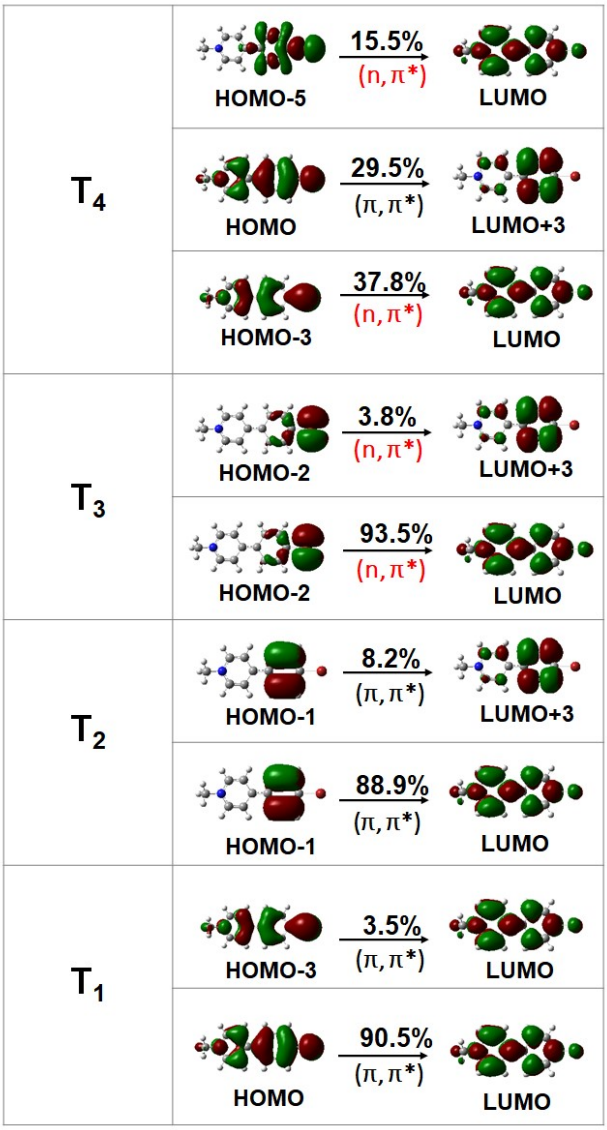


Fig. S12 Transition orbitals of the high-lying triplet states of (a) PYCl/CB[6] and (b) PYBr/CB[6].



PYCl/CB[7]



PYBr/CB[7]

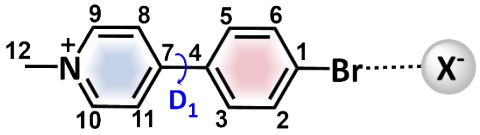
Fig. S13 Transition orbitals of the high-lying triplet states of (a) PYCl/CB[7] and (b) PYBr/CB[7].

II. Supplementary Tables

Table S1. Table of unit cell parameters and cell volume for the host-guest complexes: PYCl/CB[6], PYBr/CB[6], PYCl/CB[7], PYBr/CB[7].

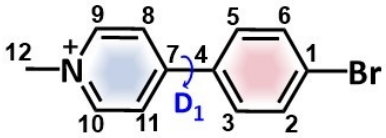
Complexes	*a* (Å)	*b* (Å)	*c* (Å)	*α*	*β*	*γ*	Volume (Å^3)
PYCl/CB[6]	20.74	13.97	10.68	90.00	120.97	90.00	2652.88
PYBr/CB[6]	20.86	13.99	10.88	90.11	121.42	89.87	2709.62
PYCl/CB[7]	12.85	20.13	31.66	90.00	92.59	90.00	8185.58
PYBr/CB[7]	12.95	19.91	32.27	89.97	91.26	89.96	8319.44

Table S2. Selected structural parameters of PYCl and PYBr at both the S_0 and T_1 geometry, the geometrical changes $|\Delta(T_1\text{-}S_0)|$ in crystal, respectively.



		PYCl			PYBr		
		S_0	T_1	$\Delta\|T_1\text{-}S_0\|$	S_0	T_1	$\Delta\|T_1\text{-}S_0\|$
	Br-X^-	3.00	2.99	0.01	3.26	3.23	0.03
	C1-Br	2.00	1.96	0.04	2.01	1.98	0.03
	C4-C7	1.48	1.41	0.07	1.48	1.41	0.07
	C2-C1-Br	120.12	120.76	0.64	119.27	119.59	0.32
	C11-C7-C4	122.13	122.61	0.48	120.17	120.07	0.10
D_1	C5-C4-C17-C11	0.70	1.08	0.38	15.91	8.13	7.78

Table S3. Selected structural parameters of PYCl/CB[6], PYBr/CB[6], PYCl/CB[7], PYBr/CB[7] at both the S_0 and T_1 geometry, the geometrical changes $|\Delta(T_1\text{-}S_0)|$ in crystal, respectively.



		PYCl/CB[6]			PYBr/CB[6]			PYCl/CB[7]			PYBr/CB[7]		
		S_0	T_1	$\Delta\|T_1\text{-}S_0\|$	S_0	T_1	$\Delta\|T_1\text{-}S_0\|$	S_0	T_1	$\Delta\|T_1\text{-}S_0\|$	S_0	T_1	$\Delta\|T_1\text{-}S_0\|$
	C1-Br	2.05	2.00	0.05	2.13	2.10	0.03	2.02	1.99	0.03	2.02	1.99	0.03
	C4-C7	1.44	1.38	0.06	1.47	1.39	0.08	1.48	1.41	0.07	1.48	1.41	0.07
	C2-C1-Br	114.72	114.59	0.13	126.32	127.27	0.95	118.31	118.61	0.30	118.21	118.75	0.74
	C11-C7-C4	120.65	120.67	0.02	121.89	122.92	1.03	120.78	121.99	1.21	120.99	122.72	1.73
D_1	C5-C4-C17-C11	1.24	1.11	0.13	1.08	2.20	1.12	34.58	1.16	33.42	29.48	6.67	22.81

Table S4. Calculated transition orbitals assignment and composition (%) of atoms in frontier molecule orbitals of PYCl, PYBr, PYCl/CB[6], PYBr/CB[6], PYCl/CB[7] and PYBr/CB[7] in S_1 state and T_1 state calculated by NAO method.

Compounds	S_1				T_1			
	Assignments	n	π	nature	Assignment	n	π	nature
PYCl	HOMO→LUMO (97%)	81.70%	16.10%	(n, π*)	HOMO-3→LUMO (42%)	47.60%	51.30%	(π, π*)
					HOMO→LUMO (36%)	89.20%	5.70%	(n, π*)
PYBr	HOMO→LUMO (98%)	79.90%	18.30%	(n, π*)	HOMO-3→LUMO (89%)	42.00%	62.10%	(π, π*)
PYCl/CB[6]	HOMO→LUMO (97%)	30.10%	64.50%	(π, π*)	HOMO→LUMO (89%)	25.60%	68.90%	(π, π*)
PYBr/CB[6]	HOMO→LUMO (98%)	28.10%	67.80%	(π, π*)	HOMO→LUMO (93%)	24.50%	71.10%	(π, π*)
PYCl/CB[7]	HOMO→LUMO (98%)	31.60%	66.10%	(π, π*)	HOMO→LUMO (94%)	29.50%	67.80%	(π, π*)
PYBr/CB[7]	HOMO→LUMO (98%)	32.10%	65.30%	(π, π*)	HOMO→LUMO (94%)	29.40%	67.70%	(π, π*)

Table S5. Calculated vertical transition energy (eV), oscillator strength (*f*), assignments and transition nature in S_n of PYCl, PYBr, PYCl/CB[6], PYBr/CB[6], PYCl/CB[7] and PYBr/CB[7].

	States	Energy (eV)	*f*	Assignments	nature
PYCl	S_1	3.06	0.0131	HOMO→LUMO (98%)	(n, π*)
	S_2	3.46	0.0001	HOMO-1→LUMO (99%)	(n, π*)
	S_3	3.48	0.0370	HOMO-2→LUMO (99%)	(n, π*)
	S_4	4.14	0.0100	HOMO-3→LUMO (95%)	(π, π*)
PYBr	S_1	2.52	0.0065	HOMO→LUMO (98%)	(n, π*)
	S_2	2.60	0.0014	HOMO-1→LUMO (99%)	(n, π*)
	S_3	2.66	0.0008	HOMO-2→LUMO (99%)	(n, π*)
	S_4	4.23	0.0040	HOMO→LUMO+1 (64%) HOMO-3→LUMO (25%)	(π, π*)
PYCl/CB[6]	S_1	3.84	0.8343	HOMO→LUMO (95%)	(π, π*)
	S_2	4.44	0.0149	HOMO-2→LUMO (58%) HOMO-1→LUMO (29%)	(n, π*)
PYBr/CB[6]	S_1	4.20	0.8619	HOMO→LUMO (95%)	(π, π*)
	S_2	4.64	0.0024	HOMO-1→LUMO (75%) HOMO→LUMO+1 (10%)	(π, π*)
	S_3	4.76	0.0020	HOMO-2→LUMO+1 (53%) HOMO→LUMO+1 (20%)	(n, π*)
PYCl/CB[7]	S_1	4.00	0.6218	HOMO→LUMO (96%)	(π, π*)
	S_2	4.35	0.0184	HOMO-1→LUMO (93%)	(π, π*)
	S_3	5.02	0.0006	HOMO-1→LUMO+1 (5%) HOMO-2→LUMO+1 (85%)	(n, π*)
PYBr/CB[7]	S_1	4.18	0.8000	HOMO→LUMO (96%)	(π, π*)
	S_2	4.47	0.0237	HOMO-1→LUMO (88%)	(π, π*)
	S_3	5.10	0.0086	HOMO→LUMO+1 (23%) HOMO-2→LUMO (63%)	(n, π*)

Table S6. The calculated properties of the excited states of PYCl, PYBr, PYCl/CB[6], PYBr/CB[6], PYCl/CB[7] and PYBr/CB[7], including oscillator strength of the S_1 ($f_{S_1-S_0}$) and the T_1($f_{T_1-S_0}$), transition dipole moment both at S_1 ($\mu_{S_1-S_0}$) and T_1 ($\mu_{T_1-S_0}$), energy gap between the S_1 and T_1 ($\Delta E_{T_1-S_0}$), spin orbit coupling constant ($\xi_{T_1-S_1}$) between the S_1 and T_1, and the ratio of $\xi_{T_1-S_1}$ to $\Delta E_{T_1-S_0}$ ($\xi_{T_1-S_1}/\Delta E_{T_1-S_1}$).

Samples	$f_{S_1-S_0}$	$f_{T_1-S_0}$ (10^{-7})	$\mu_{T_1-S_0}$ (Debye)	$\mu_{S_1-S_0}$ (Debye)	$\Delta E_{T_1-S_1}$ (eV)	$\xi_{T_1-S_1}$ (cm^{-1})	$\xi_{T_1-S_1}/\Delta E_{T_1-S_1}$ (cm^{-1}/eV)
PYCl	0.1051	0.96	0.0035	3.02	0.52	2.68	5.15
PYBr	0.0058	0.98	0.0036	0.78	0.10	1.62	16.2
PYCl/CB[6]	0.6402	6.72	0.0095	6.78	1.17	7.27	6.21
PYBr/CB[6]	0.7605	4.47	0.0080	7.04	1.51	2.29	1.51
PYCl/CB[7]	0.5049	1.14	0.0039	5.86	0.98	0.77	0.79
PYBr/CB[7]	0.7345	0.99	0.0036	6.97	1.32	0.30	0.23

Table S7. Calculated oscillator strength of the T_1 state ($f_{T_1-S_0}$), vertical excitation energy of T_1-S_0, phosphorescence wavelength of T_1 calculated at BMK/6-31G** level of PYCl, PYBr, PYCl/CB[6], PYBr/CB[6], PYCl/CB[7] and PYBr/CB[7] in crystal.

Compounds	$f_{T_1-S_0}$ (10^{-7})	$\Delta E_{T_1-S_0}$ (eV)	Emission (Cal.) (nm)	Emission (Exp.) (nm)
PYCl	0.96	2.59	478	426
PYBr	0.98	2.44	509	470
PYCl/CB[6]	6.72	2.24	554	500
PYBr/CB[6]	4.47	2.26	549	500
PYCl/CB[7]	1.14	2.25	550	482
PYBr/CB[7]	0.99	2.30	539	/

Table S8. Calculated phosphorescence radiation rate (k_P) of PYCl, PYBr, PYCl/CB[6], PYBr/CB[6], PYCl/CB[7] and PYBr/CB[7] at BMK/6-31G** level in crystal.

	PYCl	PYBr	PYCl/CB[6]	PYBr/CB[6]	PYCl/CB[7]	PYBr/CB[7]
k_p (s^{-1})	2.80×10^{1}	2.53×10^{1}	2.08×10^{2}	1.49×10^{2}	2.50×10^{1}	2.28×10^{1}

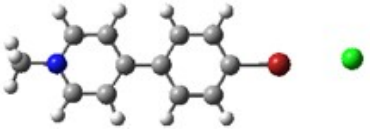
Table S9. Calculated reorganization energies (λ) of PYCl, PYBr, PYCl/CB[6], PYBr/CB[6], PYCl/CB[7] and PYBr/CB[7] in crystal at BMK/6-31G(d,p) level by AP method.

	λ (meV)
PYCl	712
PYBr	691
PYCl/CB[6]	629
PYBr/CB[6]	651
PYCl/CB[7]	932
PYBr/CB[7]	865

III. The optimized geometries and the corresponding coordinates of the QM region of the PYCl, PYBr and their complexes at both S_0 and T_1 states.

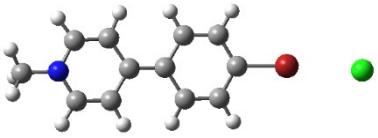
Structure S1. The optimized geometry and the corresponding coordinate of the QM region of PYCl crystal at S_0 state

Br	-0.51394900	1.83157300	0.51570800
N	-8.80106400	-1.69135800	-0.55256700
C	-10.15028600	-2.26242800	-0.61452100
H	-10.16166700	-3.10556600	-1.30402300
H	-10.85068300	-1.50848200	-0.97796900
H	-10.41008900	-2.57309600	0.39914000
C	-7.72804400	-2.45489100	-0.82811900
H	-7.92757400	-3.44575200	-1.22010100
C	-6.44380100	-1.98511000	-0.62886300
H	-5.62654800	-2.66242400	-0.85032400
C	-6.23244800	-0.67419600	-0.14608000
C	-7.39217200	0.09938700	0.10034700
H	-7.34662000	1.12499100	0.44330400
C	-8.64779300	-0.43237700	-0.09811500
H	-9.55326700	0.13317100	0.10139400
C	-4.87776500	-0.12124600	0.06266100
C	-4.71474900	1.19194100	0.54691000
H	-5.56652200	1.79513800	0.83165900
C	-3.44836600	1.74471700	0.70632900
H	-3.35150100	2.74819900	1.11125000
C	-2.32051300	0.98859100	0.37231000
C	-2.45482900	-0.32952700	-0.07521800
H	-1.57718200	-0.91715100	-0.32888300
C	-3.72611900	-0.88117600	-0.22787000
H	-3.80042100	-1.90602200	-0.57456300
Cl	2.10299900	3.26829700	0.77721300



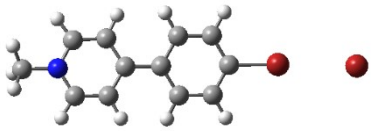
Structure S2. The optimized geometry and the corresponding coordinate of the QM region of PYCl crystal at T_1 state

Br	-0.53061100	1.84840200	0.48098200
N	-8.78272800	-1.69066500	-0.56062800
C	-10.12098000	-2.26565900	-0.60323400
H	-10.13854000	-3.11202700	-1.28948400
H	-10.83248500	-1.51710900	-0.95932200
H	-10.37923700	-2.57768700	0.41303700
C	-7.69314000	-2.46511300	-0.83899700
H	-7.89992500	-3.45344000	-1.23114300
C	-6.42081000	-2.00146400	-0.64712800
H	-5.60497100	-2.67804100	-0.87446800
C	-6.19472000	-0.65864700	-0.14927900
C	-7.39136400	0.12139200	0.10424300
H	-7.34999600	1.14757000	0.44622100
C	-8.63062100	-0.41015800	-0.09874400
H	-9.54214500	0.14693900	0.09052600
C	-4.90184500	-0.13454500	0.06496300
C	-4.71375300	1.22535600	0.58402600
H	-5.56894800	1.80217700	0.90525400
C	-3.46810900	1.76521200	0.72339300
H	-3.35998900	2.76086800	1.14617800
C	-2.30708900	1.00876200	0.36025100
C	-2.44861600	-0.34698100	-0.08328700
H	-1.56034700	-0.92232500	-0.33023800
C	-3.68747600	-0.90927000	-0.21944200
H	-3.76647000	-1.93942600	-0.54357300
Cl	2.08806800	3.26122000	0.77870000



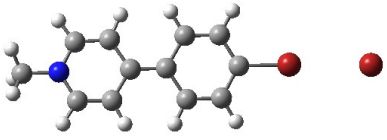
Structure S3. The optimized geometry and the corresponding coordinate of the QM region of PYBr crystal at S_0 state

Br	1.06563000	-0.48400800	0.01054200
N	-5.01001000	0.32720900	-6.70680100
C	-5.99738200	0.39529800	-7.79511100
H	-6.32192800	-0.61953700	-8.04311100
H	-6.85391200	0.98777100	-7.46774700
H	-5.54056100	0.87413300	-8.66438500
C	-5.40860400	0.42748800	-5.42368100
H	-6.46278500	0.61867800	-5.24430800
C	-4.49737800	0.30961300	-4.38993500
H	-4.87355100	0.43563300	-3.38198900
C	-3.13155600	0.07202700	-4.65649300
C	-2.75941900	-0.03480700	-6.01709600
H	-1.73638600	-0.23261200	-6.32102700
C	-3.71452900	0.09599900	-7.00494300
H	-3.47541400	0.02639700	-8.05989800
C	-2.14048500	-0.05141800	-3.56428200
C	-2.56304700	-0.26866000	-2.23572600
H	-3.61399600	-0.38119600	-1.98702000
C	-1.63467100	-0.39443300	-1.20189400
H	-1.98770700	-0.58425500	-0.19179400
C	-0.26762100	-0.31697400	-1.48974500
C	0.17220400	-0.11338700	-2.80309100
H	1.23485200	-0.06402300	-3.02686000
C	-0.75768800	0.02716000	-3.83497700
H	-0.39536200	0.21219900	-4.84309400
Br	3.15359000	-0.67239900	2.50457100



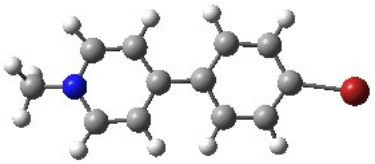
Structure S4. The optimized geometry and the corresponding coordinate of the QM region of PYBr crystal at T_1 state

Br	1.08126500	-0.48213700	0.02659500
N	-4.98407200	0.31358100	-6.68232900
C	-5.96613200	0.37580900	-7.76289000
H	-6.28812200	-0.63916200	-8.02297500
H	-6.83072300	0.95746900	-7.43445300
H	-5.51628000	0.86131800	-8.63295600
C	-5.39562500	0.35959100	-5.37891400
H	-6.45566500	0.51584300	-5.20747500
C	-4.50060600	0.22595500	-4.35264700
H	-4.89644900	0.29504400	-3.34740400
C	-3.08363100	0.05742600	-4.61212800
C	-2.70823700	0.01969200	-6.01275100
H	-1.68044000	-0.12148300	-6.32891800
C	-3.66074200	0.12488100	-6.98602500
H	-3.42600400	0.07624000	-8.04184100
C	-2.13819600	-0.07038700	-3.56952500
C	-2.55492900	-0.22233900	-2.16819000
H	-3.60568300	-0.29139900	-1.91281400
C	-1.63490500	-0.35009200	-1.16386800
H	-1.97827700	-0.50695000	-0.14409500
C	-0.23073600	-0.32910500	-1.45580500
C	0.21177200	-0.19002700	-2.81269300
H	1.27772300	-0.17713500	-3.02849800
C	-0.68980800	-0.06674900	-3.83566900
H	-0.32914600	0.05334400	-4.85215800
Br	3.14658800	-0.66739700	2.49715700



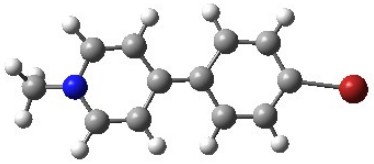
Structure S5. The optimized geometry and the corresponding coordinate of the QM region of PYCl/CB[6] crystal at S_0 state

N	-4.18580300	-0.96227200	0.90556300
C	-5.36663300	-1.08582200	1.72655400
C	-3.92885400	0.24027100	0.40499100
C	-2.61561200	0.59008500	0.20278300
C	-1.63763700	-0.37913500	0.19758100
C	-2.04113200	-1.70248000	0.33129700
C	-3.28117300	-1.94852900	0.84013100
C	-0.23892300	-0.04313100	0.10498400
C	0.67599900	-1.07964300	0.18231500
C	2.00219500	-0.80921100	0.02007200
C	2.52655300	0.43603700	-0.24109600
C	1.62148700	1.49573000	-0.09978800
C	0.25629600	1.26320800	0.03844500
Br	4.46365200	0.42701400	-0.91035400
H	-5.20676500	-0.57221000	2.67918500
H	-5.50100700	-2.14563100	1.89128300
H	-6.20712300	-0.61548900	1.23014400
H	-4.80343700	0.87131800	0.30421500
H	-2.28424200	1.60073800	0.07877900
H	-1.34438400	-2.48346100	0.14079500
H	-3.60883300	-2.89029200	1.25179100
H	0.40227800	-2.11003700	0.34157800
H	2.63110500	-1.63053900	0.10035100
H	1.92047600	2.51195500	-0.03062100
H	-0.40652400	2.12249700	0.07970900



Structure S6. The optimized geometry and the corresponding coordinate of the QM region of PYCl/CB[6] crystal at T_1 state

N	-4.17375300	-0.97749000	0.90893900
C	-5.33152200	-1.09993300	1.75047400
C	-3.92178200	0.24350900	0.39604500
C	-2.62275700	0.60288400	0.20055100
C	-1.61228100	-0.36763400	0.19197100
C	-2.02371300	-1.71813000	0.33702200
C	-3.25663500	-1.97096500	0.82928800
C	-0.26539000	-0.04035400	0.13710800
C	0.69480800	-1.09872800	0.22000400
C	1.99172400	-0.82118200	0.04452500
C	2.53755900	0.45467100	-0.22524900
C	1.60208100	1.53610600	-0.05881300
C	0.26729600	1.31219200	0.10457100
Br	4.42433000	0.42819800	-0.91303600
H	-5.18323400	-0.55050500	2.68788500
H	-5.43889100	-2.15905300	1.94858500
H	-6.19538300	-0.66794000	1.25592300
H	-4.80450700	0.86178700	0.29372900
H	-2.29345400	1.61357000	0.07245400
H	-1.32962000	-2.49455900	0.12285000
H	-3.59896300	-2.92142300	1.20437500
H	0.41694300	-2.12241100	0.39944600
H	2.63655400	-1.63102100	0.10813900
H	1.91500200	2.54744400	0.03372100
H	-0.39616900	2.16022800	0.23435400



Structure S7. The optimized geometry and the corresponding coordinate of the QM region of PYBr/CB[6] crystal at S_0 state

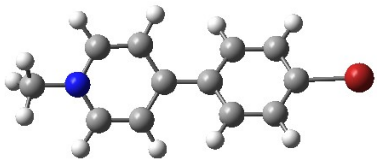
N	3.88865300	1.75911300	0.69310000
C	4.94591800	2.36432100	1.50470200
C	2.92951500	2.56368800	0.23928500
C	1.65513500	2.05532200	0.06416800
C	1.42453100	0.69927700	0.12482400
C	2.54883000	-0.11422700	0.24899900
C	3.77067800	0.42732100	0.58799000
C	0.06738400	0.13570700	0.02649800
C	-1.13238700	0.86368900	-0.11408100
C	-2.36572400	0.20512700	-0.27396200
C	-2.41816300	-1.18454400	-0.38680300
C	-1.27165400	-1.84365100	-0.01444400
C	-0.05389900	-1.23983200	0.17059600
H	5.37342300	3.24158800	1.01188900
H	5.69358200	1.59068000	1.67424900
H	4.51130100	2.67741100	2.45507400
H	3.23815800	3.59412600	0.09943900
H	0.79744100	2.68013000	-0.07583200
H	2.43436900	-1.16882600	0.15538900
H	4.66455600	-0.15041400	0.79547500
H	-1.13642000	1.95082900	-0.08479400
H	-3.28285100	0.74446600	-0.18001300
H	-1.31683700	-2.85438800	0.21965100
H	0.77691200	-1.87759500	0.43639900
Br	-4.13095900	-2.34410300	-0.87503400

Structure S8. The optimized geometry and the corresponding coordinate of the QM region of PYBr/CB[6] crystal at T_1 state

N	3.87539500	1.72736700	0.68087100
C	4.91246800	2.32416300	1.51147100
C	2.90449500	2.55216700	0.21706400
C	1.63622700	2.06809500	0.07138600
C	1.36785200	0.68451700	0.16026200
C	2.52967900	-0.14879700	0.25469600
C	3.75554200	0.38222200	0.54009100
C	0.07916300	0.15937700	0.11513100
C	-1.19635800	0.90733600	0.01802900
C	-2.38888000	0.25844900	-0.20887400
C	-2.43273200	-1.16051900	-0.42224400
C	-1.27262800	-1.84005200	0.01736200
C	-0.08379200	-1.27020400	0.27948400
H	5.35587300	3.19817400	1.02287500
H	5.65485700	1.55086700	1.70738600
H	4.46606300	2.66222300	2.44978800
H	3.22918800	3.57547300	0.06363400
H	0.77951000	2.69087800	-0.08245100
H	2.39849800	-1.20054400	0.14220000
H	4.66162900	-0.19812700	0.67833200
H	-1.20337900	1.98135000	0.18205100
H	-3.31608400	0.77991000	-0.09697200
H	-1.36034100	-2.85153300	0.23212700
H	0.71968300	-1.89568800	0.63817000
Br	-4.12165700	-2.32846700	-0.88122700

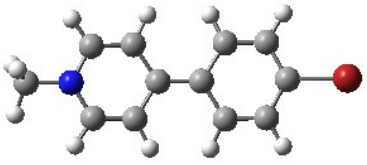
Structure S9. The optimized geometry and the corresponding coordinate of the QM region of PYCl/CB[7], S_0 state

N	-6.12123700	1.52645000	0.20749200
C	-5.27423700	1.27414300	-0.97942700
C	-5.67823500	2.33116500	1.19532300
C	-6.46501700	2.63061300	2.29572100
C	-7.77749200	2.11771600	2.38687100
C	-8.17866100	1.23711800	1.36260300
C	-7.33843300	0.95488400	0.30335600
C	-8.73047900	2.54411500	3.43501900
C	-10.08134500	2.71903700	3.08304800
C	-10.99634300	3.24098000	3.99790300
C	-10.53757600	3.57163000	5.27185000
C	-9.21769200	3.35417600	5.67270400
C	-8.30931300	2.83905900	4.74343100
H	-4.71715400	2.18703600	-1.20444300
H	-5.92064600	1.01141600	-1.81946200
H	-4.57826900	0.45248800	-0.79342700
H	-4.69003800	2.74431200	1.04351400
H	-6.08052500	3.30438400	3.05606700
H	-9.14146200	0.74755600	1.42175000
H	-7.61170900	0.26711300	-0.48607400
H	-10.43011100	2.48134800	2.08490800
H	-12.02839900	3.38780700	3.69700600
H	-8.88739800	3.57847800	6.68212800
H	-7.29312000	2.62739000	5.05972700
Br	-11.83808300	4.41348600	6.57084000



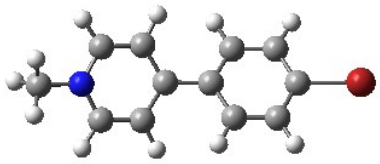
Structure S10. The optimized geometry and the corresponding coordinate of the QM region of PYCl/CB[7], T_1 state

N	-6.23385300	1.55240100	0.15580200
C	-5.34850400	1.27741500	-0.98188100
C	-5.70449900	1.74434300	1.40696600
C	-6.49830200	2.02178500	2.48717800
C	-7.93662900	2.14109400	2.34914900
C	-8.43476600	1.93346400	1.00478500
C	-7.58438700	1.65630100	-0.02881100
C	-8.79232600	2.49182300	3.41994600
C	-10.23540800	2.68766500	3.20801600
C	-11.01956500	3.27899600	4.15739900
C	-10.44130900	3.66321700	5.40486400
C	-9.08113800	3.35343300	5.72026000
C	-8.28681300	2.75815400	4.77688700
H	-4.81687400	2.19746400	-1.25415600
H	-5.94795300	0.91911500	-1.82091300
H	-4.62344700	0.50139400	-0.72544300
H	-4.62487200	1.67625800	1.46760900
H	-6.01887700	2.15238200	3.45060700
H	-9.49253800	1.99143900	0.78452100
H	-7.92709800	1.51692000	-1.04481300
H	-10.70407400	2.36855100	2.29041100
H	-12.07386200	3.43795900	3.95569200
H	-8.67712500	3.57444100	6.70378400
H	-7.27645200	2.48229900	5.04867200
Br	-11.59445400	4.57198900	6.75111400



Structure S11. The optimized geometry and the corresponding coordinate of the QM region of PYBr/CB[7], S_0 state

N	-6.06168000	1.48056800	0.27588500
C	-5.21892000	1.27696800	-0.92354800
C	-5.56928000	2.13398300	1.34710700
C	-6.36857300	2.45494200	2.43222100
C	-7.73798200	2.11351000	2.42834300
C	-8.18301800	1.33684100	1.33840400
C	-7.33442000	1.03866800	0.29052600
C	-8.68939800	2.61271000	3.44790900
C	-8.28298100	2.90889700	4.76232300
C	-9.18126800	3.49100900	5.66215400
C	-10.47756300	3.77487700	5.22861000
C	-10.92205500	3.45889700	3.94620300
C	-10.01775500	2.87284500	3.06002500
H	-5.87541000	1.20402500	-1.79345900
H	-4.62675600	0.36373300	-0.84050500
H	-4.55267800	2.13731100	-1.02354500
H	-4.52561300	2.40728500	1.27722900
H	-5.93882700	3.01446800	3.25658700
H	-9.19097500	0.94536000	1.32773300
H	-7.64162900	0.44217700	-0.55808300
H	-7.28422700	2.66169200	5.10958500
H	-8.85967600	3.71618300	6.67429800
H	-11.93475100	3.66874900	3.61795500
H	-10.35776600	2.65450100	2.05381100
Br	-11.76388100	4.69977800	6.48556800



Structure S12. The optimized geometry and the corresponding coordinate of the QM region of PYBr/CB[7], T_1 state

N	-5.94344300	1.62875300	0.33481400
C	-4.99118200	1.45073500	-0.76814400
C	-5.50119900	1.93212200	1.59364100
C	-6.36738800	2.17618900	2.62408200
C	-7.79995900	2.15686700	2.41075500
C	-8.20774700	1.73160800	1.08427300
C	-7.28539900	1.47598600	0.10862900
C	-8.72129900	2.58801000	3.39149800
C	-8.30926700	2.91740500	4.76837600
C	-9.17876700	3.52166300	5.63894800
C	-10.51487400	3.80478000	5.22161900
C	-10.99220100	3.41365000	3.93303200
C	-10.13401200	2.81173400	3.05554900
H	-5.45549700	1.82691800	-1.68414100
H	-4.73228700	0.39506900	-0.89926200
H	-4.07994600	2.01149700	-0.54548900
H	-4.42802600	1.96536200	1.70868000
H	-5.95253700	2.40764300	3.59743500
H	-9.25086300	1.57476500	0.84767200
H	-7.54920500	1.14474600	-0.88723000
H	-7.31702800	2.65911100	5.11936200
H	-8.85072900	3.76890300	6.64444100
H	-12.02111600	3.59371900	3.63757900
H	-10.50777600	2.53917300	2.08025200
Br	-11.76305800	4.74756500	6.46255400