Supporting information

Highly Efficient Ultralong Organic Phosphorescence Induced by Lone Pair Repulsions and Noncovalent Interactions

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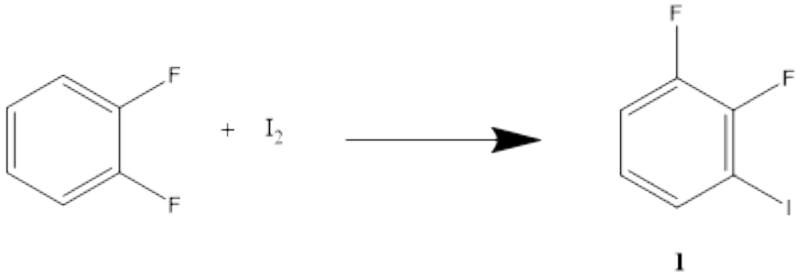
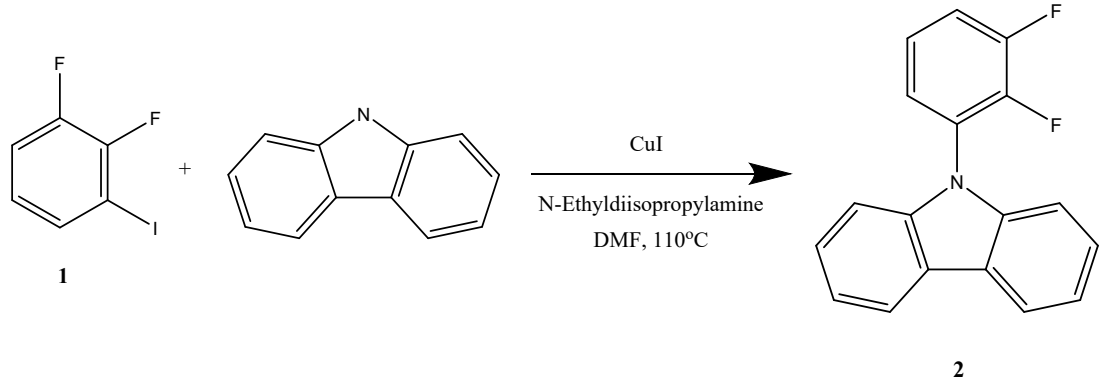
Content

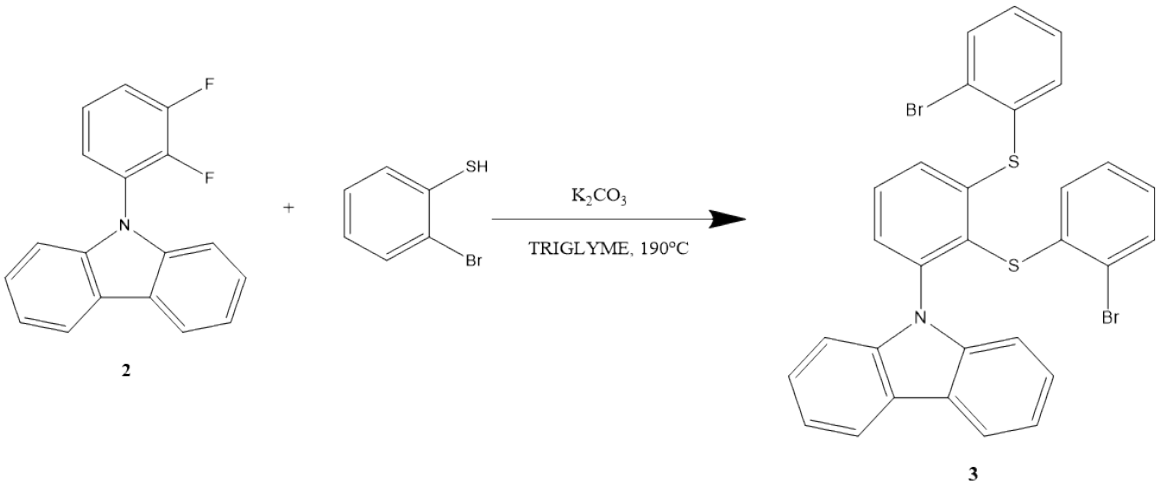
1. Synthetic schemes of Materials



Scheme S1 Synthetic route of 1,2-difluoro-3-iodobenzene



Scheme S2 Synthetic route of 9-(2,3-difluorophenyl)-9H-carbazole



Scheme S3 Synthetic route of 9-(2,3-bis((2-bromophenyl)thio)phenyl)-9H-carbazole (**BrDBTCz**)

2. NMR Spectra

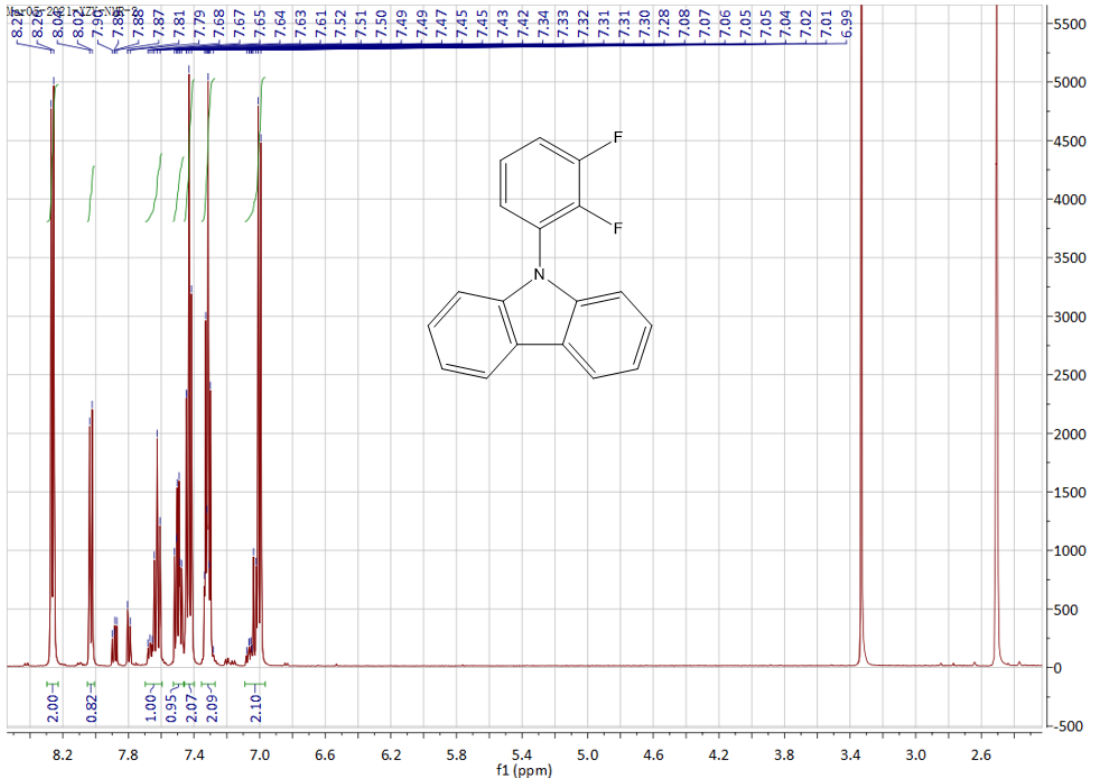


Figure S1 ^{1}H NMR spectrum of 9-(2,3-difluorophenyl)-9H-carbazole

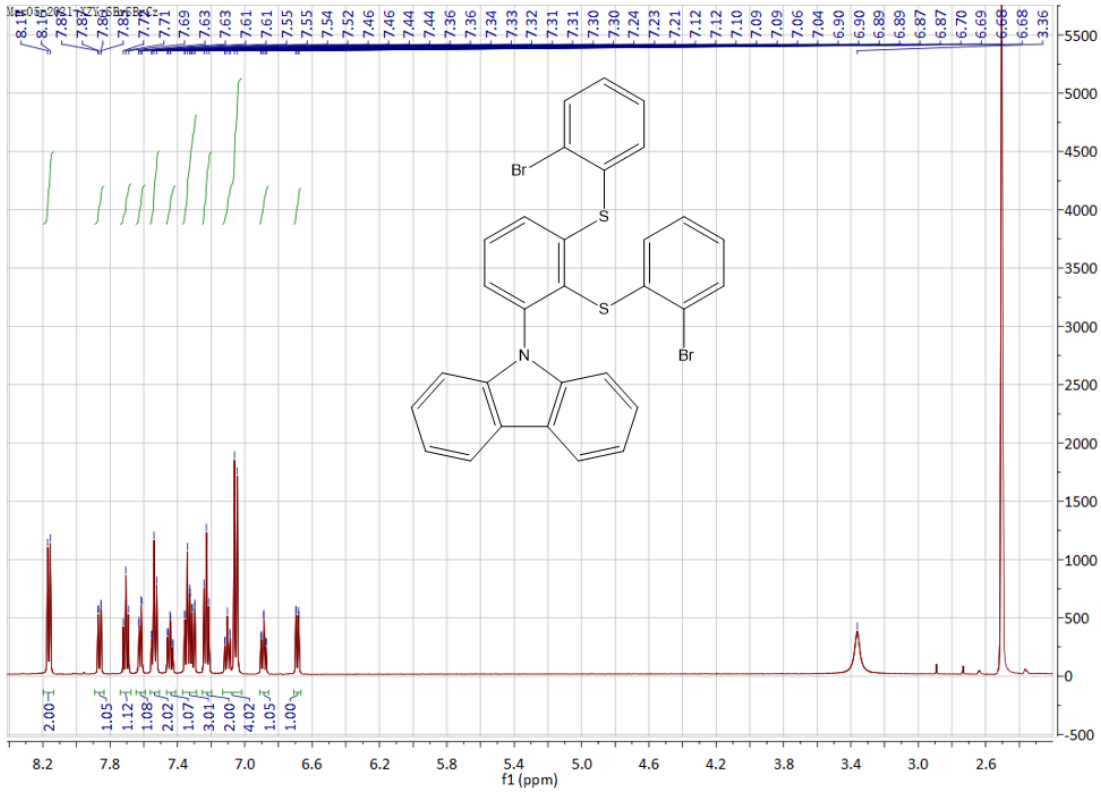


Figure S2 ^{1}H NMR spectrum of 9-(2,3-bis((2-bromophenyl)thio)phenyl)-9H-carbazole (**BrDBTCz**)

3. Single Crystals Analysis

Table S1 Single crystals data for **BrDBTCz**

Empirical formula	$C_{30}H_{19}Br_2NS_2$
Formula weight	617.40
Temperature/K	200.0
Crystal system	triclinic
Space group	*P*-1
***a* / Å**	9.2405(6)
***b* / Å**	10.8311(8)
***c* / Å**	13.7741(8)
***α* / °**	93.965(2)
***β* / °**	95.341(2)
***γ* / °**	114.128(2)
***V* / Å³**	1243.93(14)
Z	2
ρ_{calc} g/cm³	1.648
μ / mm^{-1}	3.447
***F*(000)**	616.0
Crystal size / mm³	0.192 × 0.164 × 0.09
R_{int}	0.0665
***GOOF* on F^2**	1.043
$R_1[I >= 2\sigma(I)]$	0.0413
$wR_2[I >= 2\sigma(I)]$	0.0928

Table S2 Bond lengths for **BrDBTCz**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br01	C00H	1.892(3)	C00E	C00H	1.383(4)	C008	C00K	1.385(5)
Br02	C008	1.900(3)	C00E	C00N	1.410(4)	C009	C00P	1.394(4)
S003	C006	1.773(3)	C00F	C00J	1.412(4)	C00A	C00B	1.377(4)
S003	C009	1.770(3)	C00F	C00L	1.380(5)	C00B	C00I	1.388(4)
S004	C007	1.768(3)	C00G	C00J	1.441(5)	C00C	C00I	1.387(4)
S004	C00E	1.772(3)	C00G	C00U	1.395(5)	C00D	C00G	1.409(4)
N005	C00C	1.422(4)	C00H	C00O	1.385(4)	C00D	C00Q	1.388(5)
N005	C00D	1.387(4)	C00J	C00W	1.401(5)	C00P	C00T	1.382(5)
N005	C00F	1.396(4)	C00K	C00R	1.377(5)	C00Q	C00V	1.388(5)
C006	C007	1.407(4)	C00L	C00Y	1.389(5)	C00R	C00T	1.368(5)
C006	C00C	1.400(4)	C00M	C00O	1.379(5)	C00U	C00X	1.369(5)
C007	C00A	1.391(4)	C00M	C00S	1.378(5)	C00V	C00X	1.400(5)
C008	C009	1.386(4)	C00N	C00S	1.373(4)	C00W	C00Z	1.369(6)

Table S3 Bond angles for **BrDBTCz**

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C009	S003	C006	102.44(14)	C00L	C00F	N005	129.2(3)
C007	S004	C00E	103.44(14)	C00L	C00F	C00J	122.5(3)
C00D	N005	C00C	125.5(3)	C00D	C00G	C00J	106.8(3)
C00D	N005	C00F	108.8(2)	C00U	C00G	C00D	118.9(3)
C00F	N005	C00C	125.6(3)	C00U	C00G	C00J	134.3(3)
C007	C006	S003	121.8(2)	C00E	C00H	Br01	120.7(2)
C00C	C006	S003	119.1(2)	C00E	C00H	C00O	121.3(3)
C00C	C006	C007	119.0(3)	C00O	C00H	Br01	118.1(2)
C006	C007	S004	117.7(2)	C00C	C00I	C00B	119.5(3)
C00A	C007	S004	122.8(2)	C00F	C00J	C00G	107.1(3)
C00A	C007	C006	119.5(3)	C00W	C00J	C00F	118.5(3)
C009	C008	Br02	120.4(2)	C00W	C00J	C00G	134.4(3)
C00K	C008	Br02	117.9(3)	C00R	C00K	C008	119.3(3)
C00K	C008	C009	121.7(3)	C00F	C00L	C00Y	117.3(3)
C008	C009	S003	120.2(2)	C00S	C00M	C00O	119.9(3)
C008	C009	C00P	117.7(3)	C00S	C00N	C00E	120.7(3)
C00P	C009	S003	122.1(2)	C00M	C00O	C00H	119.9(3)
C00B	C00A	C007	120.7(3)	C00T	C00P	C009	120.7(3)
C00A	C00B	C00I	120.6(3)	C00V	C00Q	C00D	117.4(3)
C006	C00C	N005	120.2(3)	C00T	C00R	C00K	120.2(3)
C00I	C00C	N005	119.0(3)	C00N	C00S	C00M	120.4(3)
C00I	C00C	C006	120.8(3)	C00R	C00T	C00P	120.5(3)
N005	C00D	C00G	108.9(3)	C00X	C00U	C00G	119.3(3)
N005	C00D	C00Q	128.9(3)	C00Q	C00V	C00X	120.9(3)
C00Q	C00D	C00G	122.2(3)	C00Z	C00W	C00J	119.3(3)
C00H	C00E	S004	124.4(2)	C00U	C00X	C00V	121.2(3)
C00H	C00E	C00N	117.8(3)	C00L	C00Y	C00Z	121.2(4)
C00N	C00E	S004	117.6(2)	C00W	C00Z	C00Y	121.2(3)
N005	C00F	C00J	108.3(3)				

4. UV-Vis Analysis and Thermogravimetry

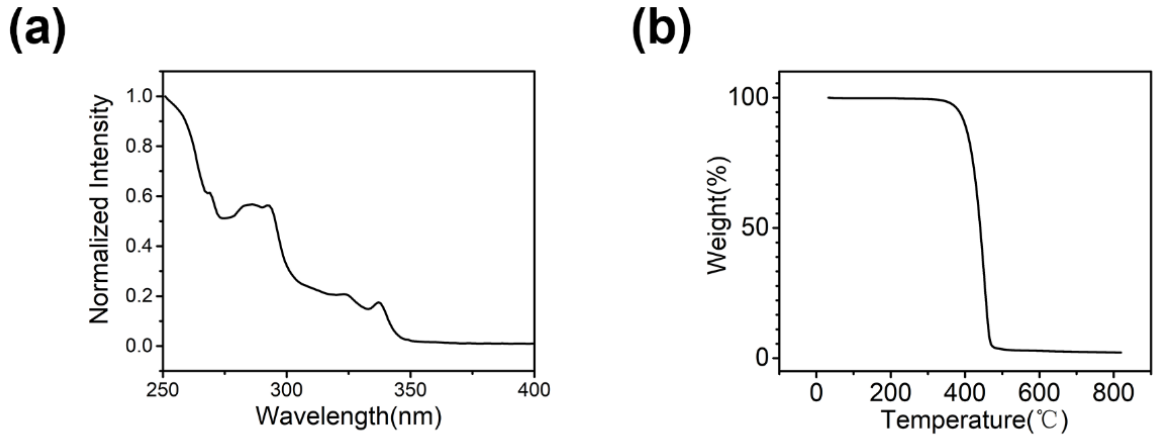


Figure S3 (a) UV-vis absorption spectrum of **BrDBTCz** in 2-MeTHF solution; (b) TGA curve of **BrDBTCz**.

5. Photophysical Properties

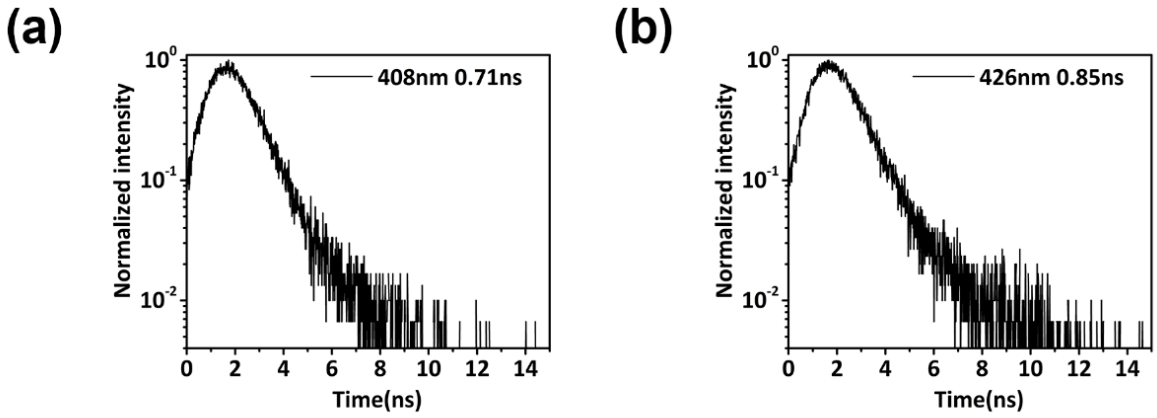


Figure S4 Time-resolved fluorescence decay curves of crystalline **BrDBTCz** at 298K.

Table S4 Photoluminescence lifetimes and percentages (*A*) of crystalline **BrDBTCz** under ambient conditions

Fluorescence		Room Temperature Phosphorescence				
Wavelength(nm)	τ_1 (ns)	Wavelength(nm)	τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)
408	0.71	550	89.5	41.3	367	58.7
		596	82.6	47.9	343	52.1
426	0.85	650	75.1	67.5	322	32.5

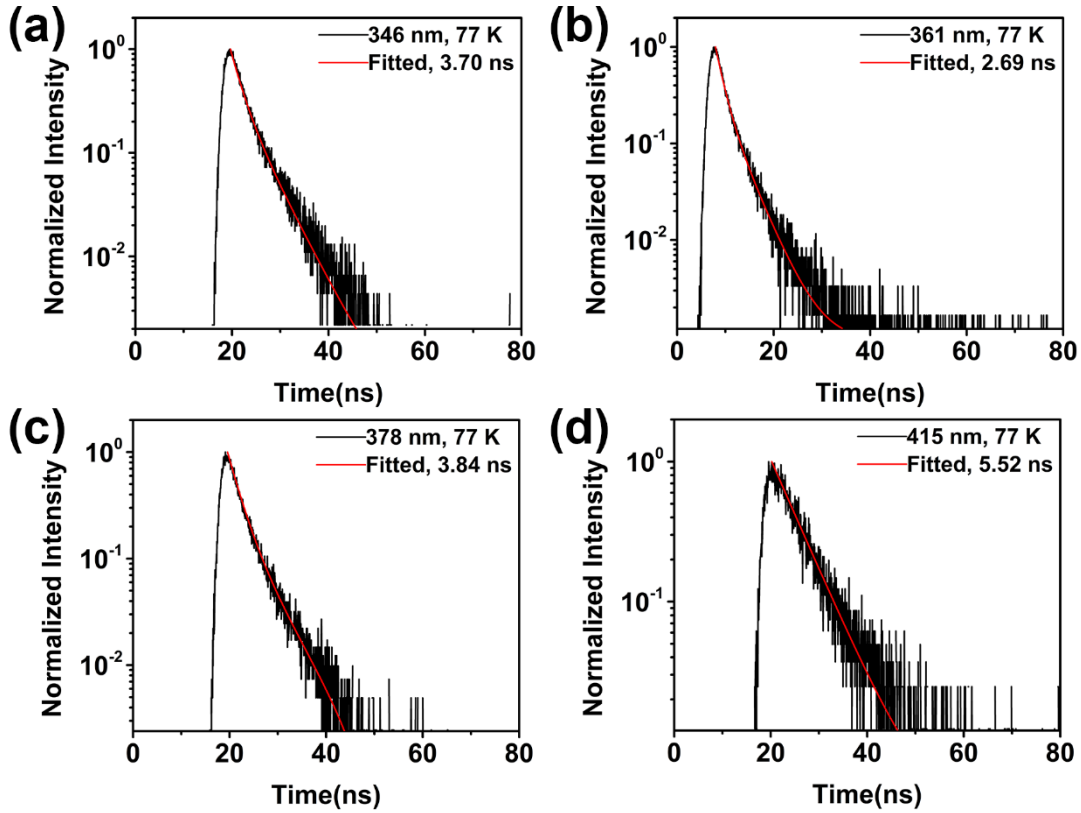


Figure S5 Time-resolved emission decay curves of **BrDBTCz** in a diluted 2-MeTHF solution at 77 K.

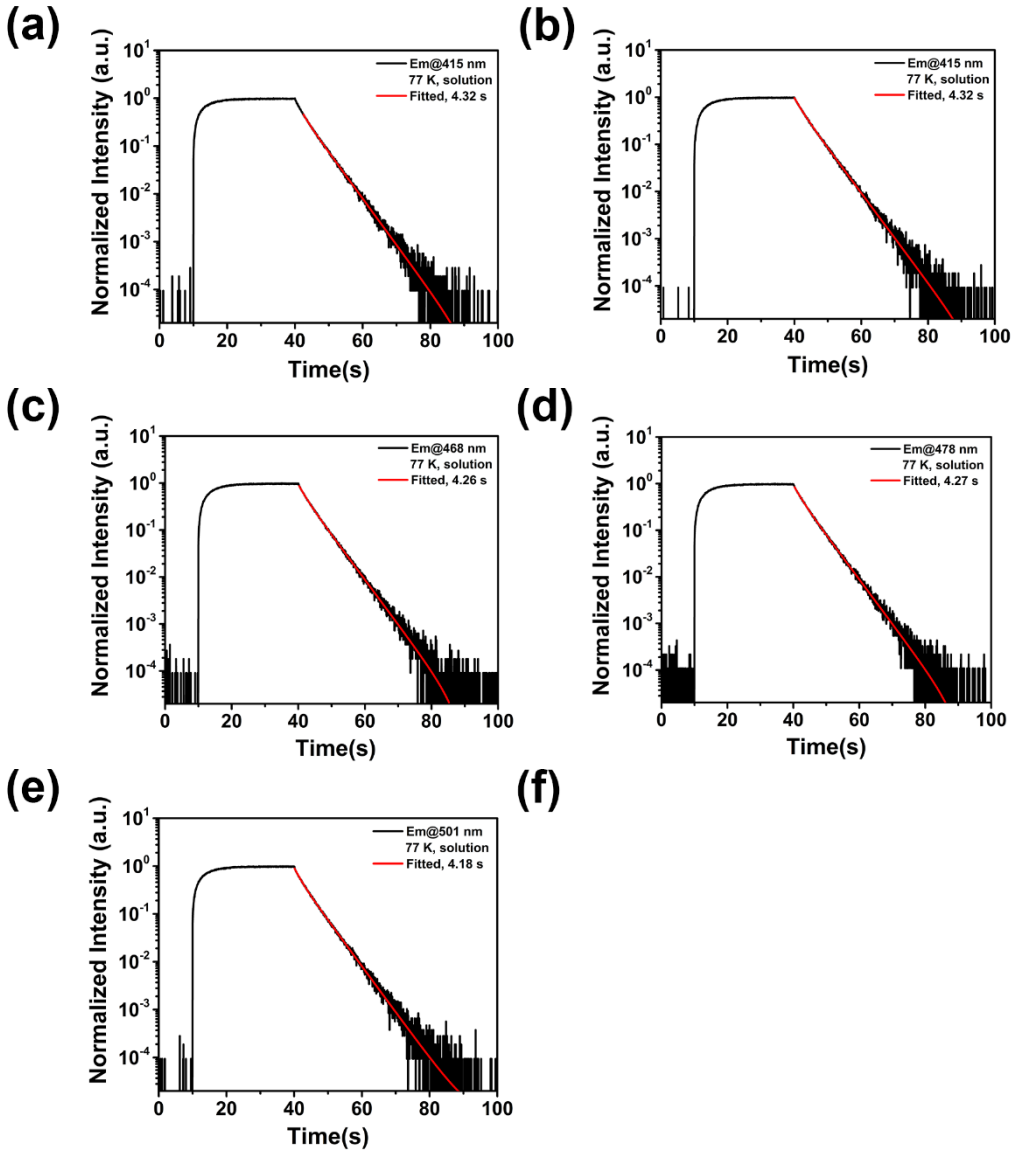


Figure S6 Phosphorescence decay curves at 77 K of **BrDBTCz** in diluted 2-MeTHF solution.

Table S5 Photoluminescence lifetimes of **BrDBTCz** in the solution of 2-MeTHF at 77 K

Wavelength (nm)	Flourescence				Ultralong Phosphorescesnce			
	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_1 (s)	A_1 (%)	τ_2 (s)	A_2 (%)
346	1.98	39.7	4.83	60.3				
361	1.48	46.7	3.75	53.3				
378	2.34	58.1	5.92	41.9				
415	5.52	100	—	—	1.69	5.9	4.49	94.1
444					1.89	11.1	4.57	88.9
468					1.89	11.2	4.56	88.8
478					1.9	11.3	4.57	88.7
501					1.7	11.8	4.51	88.2

Table S6 Photophysical parameters of crystalline **BrDBTCz** under the excitation of 400 nm at 298 K

Φ_{total} [a] (%)	Fluorescence				Phosphorescence				
	$\overline{\tau}_F$ [b] (ns)	Φ_F [c] (%)	k^F_r (× 10^7 s^{-1})	k^F_{nr} (× 10^7 s^{-1})	$\overline{\tau}_P$ [d] (ms)	Φ_P [e] (%)	k^P_r (s^{-1})	k^P_{nr} (s^{-1})	k_{ISC}[1] (× 10^7 s^{-1})
21.51	0.63	2.51	3.98	124.59	209	19.00	0.91	3.87	30.16

[a] Absolute photoluminescence quantum yield from 385–660 nm;

[b] Algorithmic average lifetime value of all the main fluorescent emission peaks;

[c] $\Phi_F = \Phi_{total} - \Phi_P$

[d] Algorithmic average lifetime value of all the main phosphorescent emission peaks;

[e] photoluminescence quantum yield from 500–660 nm;

Note [1] Reference: Zhao, W., et al. Boosting the efficiency of organic persistent room-temperature phosphorescence by intramolecular triplet-triplet energy transfer, *Nat. Commun.*, **2019**, *10*, 1595–1603.

$k^F_r = \Phi_F / \tau_F$; $k^F_{nr} = (1 - \Phi_F - \Phi_P) / \tau_F$;

$k^P_r = \Phi_P / \tau_P$; $k^P_{nr} = (1 - \Phi_P) / \tau_P$

$k_{ISC} = \Phi_P / \tau_F$

6. Data for reference compound

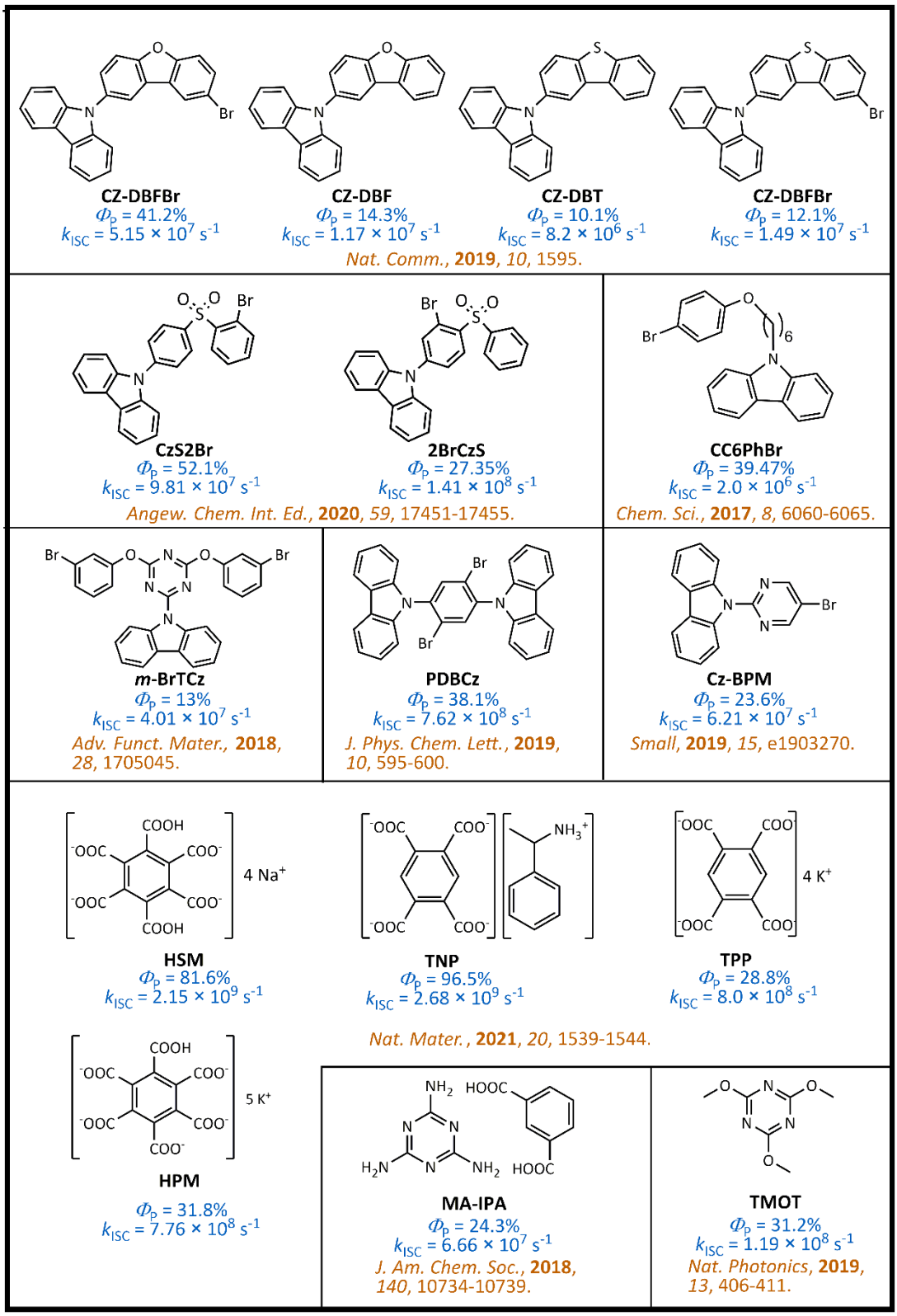


Figure S7 A list of the reported non-doped pure organic phosphors with phosphorescent quantum yield over 10%, in which the phosphorescent quantum yield (Φ_p), intersystem crossing constant (k_{ISC}) and the reference of each molecule was noted underneath, correspondingly

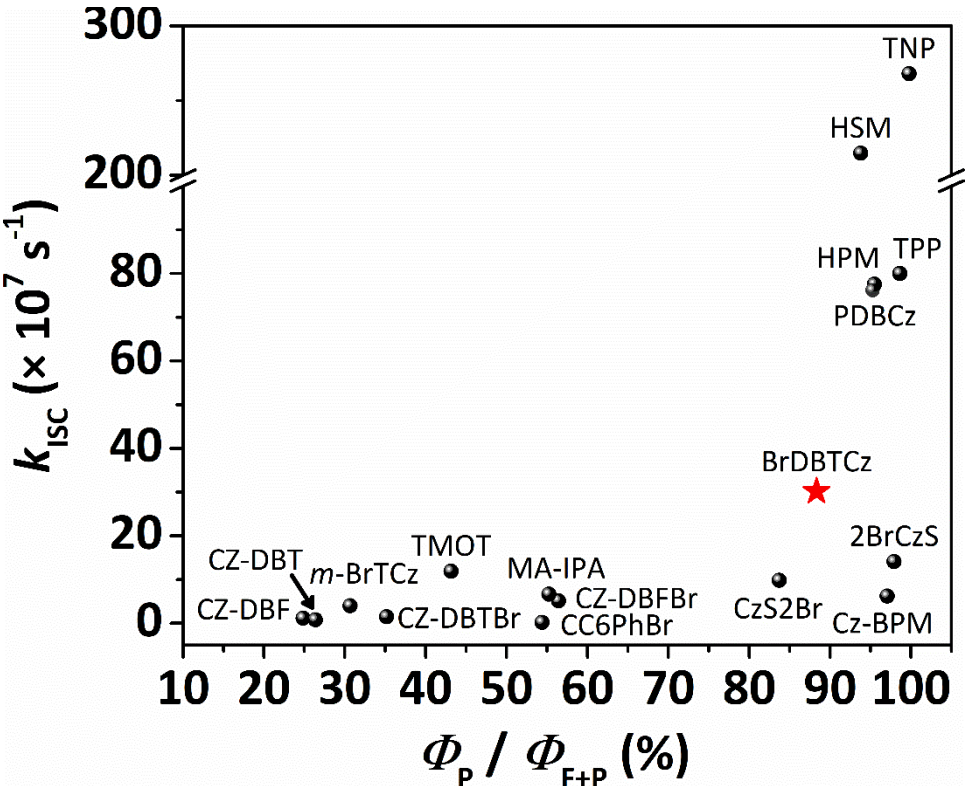


Figure S8 The diagram of the reported non-doped pure organic phosphors with phosphorescent quantum yield over 10%, in which the names are identical to that in **Figure S7**.

7. Theoretical Calculation

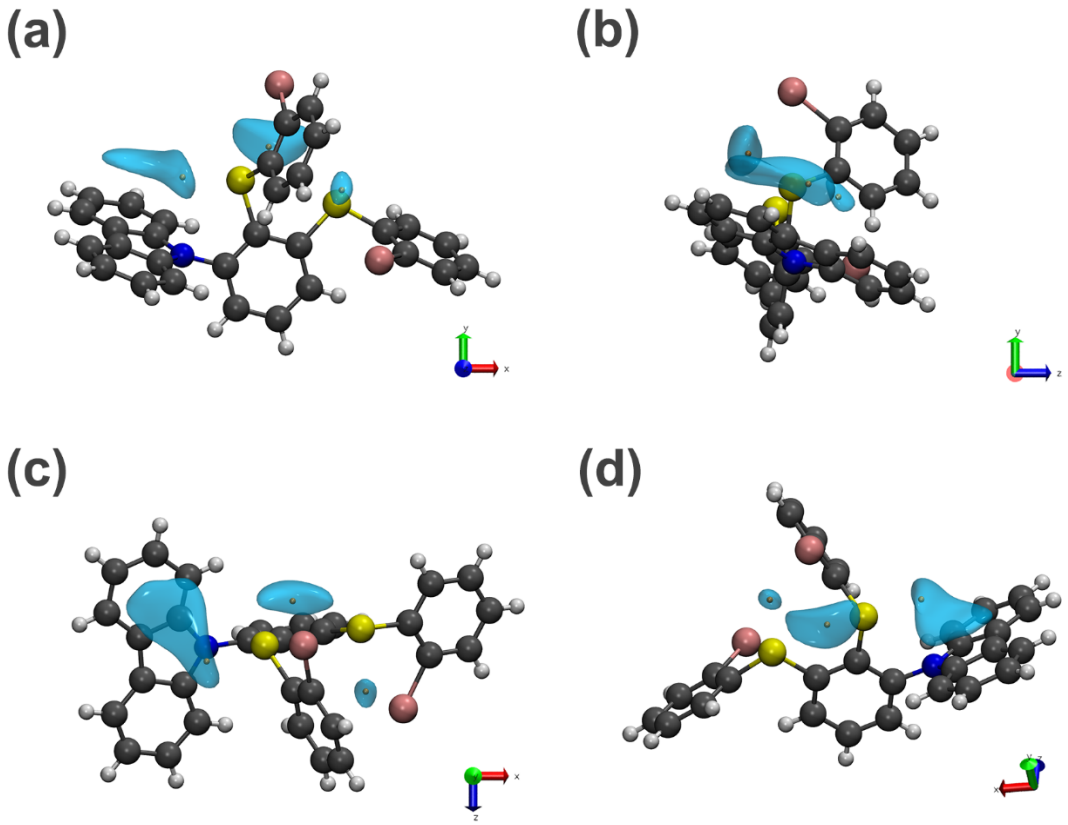
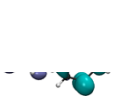
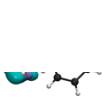
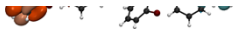
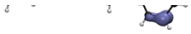
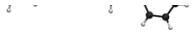


Figure S9 The molecular electro-static potential (MESP) isosurface painted in blue translucent block visualizes the lone pair regions of sulphur atoms (with π electrons from carbazole group), in which the brown point inside the block indicated the attractor (minimum point). The isovalue is for the surface is 0.09 atom unit (a.u.) higher than the minimum ESP value. Axes colouring in red, green and blue represent *x*, *y* and *z* axis, respectively

Table S7 Frontier orbitals (HOMO: blue, LUMO: orange), and electron (green) / hole (purple) densities of excited states S_1 and T_1 for single **BrDBTCz** molecule and its six dimers, with ΔE_{ST} and

	Ground State (S_0)	The Lowest Excited Singlet State (S_1)	The Lowest Excited Triplet State (T_1)	ΔE_{ST} / eV	μ^2 ($T_1 \rightarrow S_0$)
Single Molecule				0.58	20.95
Dimer 1				0.53	167.04
Dimer 2				0.71	3027.13
Dimer 3				0.50	21.21
Dimer 4				0.61	18.30
Dimer 5				0.54	40.89
Dimer 6				0.55	25.11

SOC coefficient(ξ) listed correspondingly.

Table S8 Energy level of HOMO, LUMO and their bandgap of monomer and dimer **BrDBTCz**

	Monomer	Dimer 1	Dimer 2	Dimer 3	Dimer 4	Dimer 5	Dimer 6
HOMO (eV)	-5.5511	-5.5124	-5.5857	-5.3853	-5.6041	-5.7150	-5.4592
LUMO (eV)	-1.3126	-1.3622	-1.2107	-1.3909	-1.3151	-1.4326	-1.2635
Bandgap (eV)	4.2385	4.1502	4.3750	3.9944	4.2890	4.2824	4.1957

Table S9 Component analysis of the excited-state **BrDBTCz** monomer

State	No.	Energy (eV)	Transition Contributions (%)[a]	ξ_{Tn-S1} (cm^{-1})
S_n	1	3.7333	H→L+1(89.00%), H→L+2(5.93%)	--
	2	3.8389	H→L(89.78%), H→L+4(3.48%)	
	3	4.0020	H→L+3(64.43%), H-2→L(10.44%), H-3→L(7.84%), H-1→L(6.71%)	
	4	4.0193	H-2→L(27.19%), H→L+3(22.45%), H-3→L(17.24%), H-1→L(10.58%), H→L+4(8.61%), H-1→L+1(6.98%)	
	5	4.0490	H-1→L+1(58.45%), H-2→L+1(9.94%), H→L+4(8.34%), H-2→L(4.25%), H-1→L(3.59%), H-1→L+2(3.36%), H→L(3.22%)	
T_n	1	3.1554	H-1→L+3(57.01%), H-1→L+4(19.00%), H→L+9(6.37%)	0.45
	2	3.3038	H-2→L+1(36.24%), H-2→L+2(8.81%), H-3→L+4(7.72%), H-3→L+5(3.68%), H-3→L(3.48%), H→L+3(3.48%)	1.77
	3	3.3611	H→L+3(70.12%), H→L+4(16.28%)	0.98
	4	3.5060	H-2→L+5(18.39%), H-2→L(8.29%), H-3→L+1(7.60%), H-4→L+6(5.83%), H-3→L+6(4.74%), H-4→L+5(4.67%), H-4→L+4(3.90%), H-7→L+5(3.74%), H-2→L+1(3.59%), H-2→L+6(3.53%), H-4→L+7(3.38%)	0.90
	5	3.5727	H-3→L(27.31%), H-9→L(16.65%), H-6→L+2(9.10%), H-2→L(8.58%), H-6→L(8.19%), H-6→L+1(4.07%)	1.11
	6	3.6597 (ΔE_{S1Tn}=0.0736)	H→L+1(73.01%), H→L+4(9.11%), H-3→L+1(4.69%), H→L+2(4.14%)	1.33
	7	3.7773 (ΔE_{S1Tn}=0.0440)	H→L(39.80%), H-2→L+1(12.23%), H→L+4(7.36%), H→L+1(6.92%), H-3→L+4(3.94%), H-2→L+4(3.10%)	4.74
	8	3.8754	H→L(47.20%), H-2→L+1(9.94%), H-2→L+4(9.76%), H-3→L+4(9.70%), H-2→L+3(4.11%)	2.74
	9	3.9758	H-3→L+1(43.80%), H-2→L(10.43%), H→L+4(6.60%), H-1→L(4.06%), H-6→L+1(3.05%)	3.40
	10	3.9924	H→L+4(16.90%), H-3→L+1(12.75%), H-2→L(9.39%), H-2→L+4(5.80%), H-1→L(5.36%), H-3→L(4.57%), H→L+3(4.54%), H-6→L+2(4.44%), H→L+1(3.97%), H-2→L+3(3.32%)	2.40

[a] H: HOMO ; L: LUMO

Table S10 Component analysis of the excited-state **BrDBTCz** configurated as dimer 1

State	No.	Energy (eV)	Transition Contributions (%)[a]	ξ_{Tn-S1} (cm^{-1})
S_n	1	3.6588	H-1→L+2(50.00%), H-1→L+1(39.07%), H-1→L+4(4.84%), H-1→L+5(3.36%)	--
	2	3.6747	H-1→L+1(48.91%), H-1→L+2(36.69%), H-1→L(9.83%)	
	3	3.7514	H→L+3(91.75%), H→L+9(3.14%)	
	4	3.7744	H-1→L(78.65%), H-1→L+1(6.07%), H-1→L+5(4.85%), H-1→L+2(4.42%)	
	5	3.8845	H→L+1(51.69%), H→L+2(27.35%), H→L(3.19%)	
	6	3.9206	H-3→L+1(37.29%), H-3→L+2(18.75%), H-2→L+1(16.22%), H-2→L+2(8.37%), H-3→L(4.61%), H-1→L+3(3.12%)	
	7	3.9473	H-1→L+3(48.97%), H-1→L+5(25.30%), H-1→L+7(3.94%), H-3→L+1(3.61%), H-1→L(3.23%)	
	8	3.9762	H-3→L+2(37.90%), H-1→L+3(13.52%), H-3→L+1(13.50%), H-2→L+2(12.93%), H-2→L+1(5.25%)	
	9	3.9834	H-1→L+5(28.97%), H-1→L+3(12.40%), H-3→L(8.28%), H-5→L(6.88%), H-3→L+1(6.58%), H-7→L(5.86%), H-3→L+2(5.25%), H-2→L+2(3.50%)	
	10	3.9955	H→L(91.80%), H→L+6(3.02%)	
T_n	1	3.1273	H-3→L+8(21.27%), H-3→L+7(13.55%), H-3→L+1(9.47%), H-3→L+2(8.27%), H-2→L+8(7.37%), H-1→L+18(4.90%), H-2→L+7(4.73%), H-2→L+1(3.31%)	0.44
	2	3.1558	H-2→L+6(40.39%), H-3→L+6(14.63%), H-2→L+8(7.71%), H→L+19(5.44%), H-2→L+9(5.13%)	0.00
	3	3.2888	H-5→L+2(12.75%), H-5→L+1(11.20%), H-1→L+2(11.09%), H-7→L+5(6.42%), H-5→L+4(5.72%), H-1→L+1(5.37%), H-1→L+8(5.18%), H-1→L+7(4.55%), H-1→L+5(3.29%)	1.57
	4	3.3011	H-4→L+3(34.83%), H-4→L+7(6.49%), H-6→L+9(3.41%)	0.40
	5	3.3135	H-1→L+8(16.91%), H-1→L+2(15.29%), H-1→L+1(12.34%), H-1→L+7(11.74%), H-5→L+1(5.37%), H-5→L+2(4.68%), H-4→L+3(3.30%)	0.92
	6	3.3576	H→L+6(66.98%), H→L+8(10.64%), H→L+9(5.22%), H→L+7(4.15%)	0.00
	7	3.4994	H-6→L+3(12.28%), H-4→L+11(11.81%), H-6→L+11(5.96%), H-6→L+13(5.77%), H-9→L+13(4.81%), H-4→L+1(3.73%), H-6→L+6(3.51%), H-8→L+13(3.03%)	0.09
	8	3.5038	H-5→L+10(15.57%), H-5→L(7.37%), H-7→L+12(4.22%), H-5→L+12(4.12%), H-7→L+1(3.90%), H-8→L+10(3.17%), H-8→L+12(3.14%), H-5→L+1(3.03%), H-7→L+2(3.02%)	0.89

State	No.	Energy (eV)	Transition Contributions (%)[a]	ξ_{Tn-S1} (cm^{-1})
T_n	9	3.5592	H-6→L+1(9.89%), H-12→L+7(8.74%), H-4→L+1(7.63%), H-6→L+2(6.60%), H-4→L+2(5.22%), H-12→L+9(5.22%), H-16→L+1(3.40%), H-14→L+1(3.08%)	0.08
	10	3.5742	H-7→L(27.59%), H-19→L(16.43%), H-13→L+4(8.84%), H-13→L(8.09%), H-5→L(7.48%)	0.72
	11	3.5932 (ΔE_{S1Tn}=0.0656)	H-1→L+1(43.45%), H-1→L+2(35.84%), H-1→L+5(4.44%), H-1→L+4(4.12%)	1.00
	12	3.6665	H→L+3(69.34%), H→L+9(8.02%), H-6→L+3(5.37%), H-4→L+3(4.41%)	0.15
	13	3.7066 (ΔE_{S1Tn}=0.0478)	H-1→L(49.48%), H-1→L+5(9.69%), H-1→L+1(6.30%), H-1→L+8(5.63%), H-5→L+2(4.76%)	4.57
	14	3.7801	H-4→L+3(15.62%), H→L+3(12.23%), H→L+1(8.59%), H-1→L+3(5.64%), H-4→L+9(5.12%), H→L+2(4.12%), H→L+7(3.75%)	0.88
	15	3.8175	H-1→L+1(19.18%), H-1→L+2(17.89%), H-1→L+8(15.03%), H-1→L+7(11.75%), H-1→L(11.14%)	1.60
	16	3.8404	H-1→L(24.25%), H-7→L+5(13.72%), H-5→L+5(13.12%), H-5→L+2(12.20%), H-1→L+5(5.02%), H-3→L+2(3.49%)	2.53
	17	3.8913	H→L+1(40.70%), H→L+2(22.28%), H-1→L+3(4.21%), H-4→L+9(4.16%)	0.26
	18	3.9114	H-3→L+1(22.92%), H-2→L+1(10.71%), H-3→L+2(9.44%), H-3→L(7.61%), H-1→L+18(6.37%), H-2→L+2(4.63%), H-2→L(3.06%)	0.83
	19	3.9347	H-1→L+3(31.03%), H-1→L+5(17.16%), H-1→L+9(4.33%), H-6→L+3(3.86%)	0.98
	20	3.9532	H-1→L+5(20.17%), H-6→L+3(9.12%), H-3→L+1(7.17%), H-2→L+1(5.92%), H-3→L+2(3.80%), H-5→L(3.78%), H-5→L+5(3.30%)	2.04

[a] H: HOMO ; L: LUMO

Table S11 Component analysis of the excited-state **BrDBTCz** configurated as dimer 2

State	No.	Energy (eV)	Transition Contributions (%)[a]	ξ_{Tn-S1} (cm^{-1})
S_n	1	3.8670	H→L+2(24.71%), H-1→L+2(24.30%), H→L+3(20.74%), H-1→L+3(17.10%)	--
	1d[b]	3.8674	H→L+2(24.82%), H-1→L+2(23.83%), H-1→L+3(20.11%), H→L+3(18.04%)	
	3	3.9503	H→L+1(31.33%), H-1→L(26.81%), H→L(8.55%), H-6→L(7.25%), H-7→L+1(4.95%), H-2→L+1(3.68%)	
	4	3.9509	H→L(32.32%), H-1→L+1(27.98%), H→L+1(7.45%), H-6→L+1(6.88%), H-7→L(4.60%), H-2→L(3.67%)	
	5	3.9940	H-1→L+4(46.70%), H→L+5(41.41%)	
	6	3.9956	H→L+4(47.84%), H-1→L+5(39.06%)	
	7	4.0297	H-2→L(20.15%), H-1→L+1(18.34%), H-6→L+1(11.25%), H-7→L(8.33%), H-5→L+1(7.25%), H-3→L+1(7.08%), H-4→L(6.55%), H→L+9(3.93%), H-1→L+8(3.54%)	
	8	4.0334	H-1→L(19.85%), H-2→L+1(19.72%), H-6→L(11.05%), H-7→L+1(8.53%), H-5→L(7.34%), H-4→L+1(6.84%), H-3→L(6.59%), H-1→L+9(3.85%), H→L+8(3.58%)	
	9	4.0591	H-2→L+2(41.08%), H-3→L+3(13.99%), H-5→L+3(12.76%), H-4→L+2(11.23%)	
	10	4.0730	H-2→L+3(29.20%), H-3→L+2(17.40%), H-5→L+2(16.63%), H-1→L+1(9.10%), H-4→L+3(8.35%), H→L+3(3.20%)	
T_n	1	3.1575	H-3→L+4(15.83%), H-2→L+5(11.92%), H-3→L+5(11.88%), H-4→L+5(11.82%), H-4→L+4(7.68%), H-2→L+4(7.65%), H-5→L+4(4.82%), H-5→L+5(3.54%)	0.09
	1d[b]	3.1578	H-3→L+5(17.20%), H-3→L+4(11.01%), H-2→L+4(10.86%), H-4→L+4(10.09%), H-2→L+5(8.17%), H-4→L+5(7.50%), H-5→L+5(6.21%), H-5→L+4(4.04%)	0.41
	3	3.2966	H-5→L+2(10.04%), H-2→L+3(9.07%), H-7→L+9(6.43%), H-4→L+3(6.19%), H-3→L+2(4.66%), H-6→L+8(3.67%)	1.90
	4	3.2971	H-2→L+2(10.23%), H-5→L+3(8.16%), H-4→L+2(7.42%), H-6→L+9(6.32%), H-3→L+3(3.93%), H-7→L+8(3.73%)	0.82
	5	3.3373	H→L+5(40.84%), H-1→L+4(38.60%)	0.64
	6	3.3377	H-1→L+5(40.72%), H→L+4(37.86%)	0.26
	7	3.4762	H-8→L+10(7.57%), H-5→L+10(5.98%), H-2→L+13(5.70%), H-8→L+8(5.35%), H-5→L+11(5.04%), H-4→L+13(4.82%), H-9→L+15(4.28%), H-6→L+2(3.66%)	0.78
	8	3.5107	H-5→L+13(10.54%), H-8→L+15(5.63%), H-2→L+10(4.33%), H-3→L+13(3.75%), H-9→L+10(3.55%), H-4→L+10(3.31%)	1.04
	9	3.5675	H-6→L+1(15.75%), H-7→L(15.29%), H-17→L(8.74%), H-16→L+1(7.84%), H-13→L+7(4.22%), H-13→L(3.10%)	1.30

State	No.	Energy (eV)	Transition Contributions (%)[a]	ξ_{Tn-S1} (cm^{-1})
T_n	10	3.5691	H-7→L+1(14.97%), H-6→L(14.81%), H-17→L+1(8.48%), H-16→L(7.78%), H-13→L+6(4.04%), H-13→L+1(3.13%)	1.00
	11	3.7492	H→L+2(19.33%), H-1→L+3(13.26%), H→L+8(5.79%), H-6→L+3(5.30%), H-7→L+2(5.24%), H→L+3(4.77%), H-1→L+9(4.06%), H-1→L+2(3.97%)	2.49
	12	3.7497	H→L+3(16.57%), H-1→L+2(15.97%), H-6→L+2(5.73%), H-1→L+8(4.96%), H→L+2(4.77%), H-7→L+3(4.58%), H→L+9(4.53%), H-1→L+3(3.98%), H-7→L+9(3.08%)	1.09
	13	3.8177 (ΔE_{S1Tn}=0.0493)	H-1→L+2(16.47%), H→L+3(8.61%), H-2→L+3(6.75%), H-7→L+9(5.93%), H-6→L+8(5.11%), H-5→L+2(4.71%), H-4→L+3(3.89%), H-2→L+9(3.56%), H→L(3.19%)	2.47
	14	3.8184 (ΔE_{S1Tn}=0.0486)	H-1→L+3(14.34%), H→L+2(10.68%), H-2→L+2(7.25%), H-6→L+9(6.82%), H-2→L+8(4.31%), H-4→L+2(4.19%), H-5→L+3(4.08%), H-7→L+8(3.52%)	1.34
	15	3.9451	H→L+1(19.69%), H-1→L(17.78%), H-7→L+2(7.51%), H-6→L+3(6.44%), H→L(5.24%), H-2→L+8(3.34%)	2.36
	16	3.9456	H→L(19.67%), H-1→L+1(17.49%), H-6→L+2(7.53%), H-7→L+3(7.43%), H→L+1(4.53%)	1.02
	17	3.9724	H-6→L+2(17.23%), H-7→L+3(15.68%), H-1→L+1(14.69%), H→L(9.61%), H-1→L(3.02%)	3.66
	18	3.9730	H-7→L+2(16.90%), H-6→L+3(15.18%), H-1→L(14.03%), H→L+1(9.11%), H-2→L+1(3.60%), H-1→L+1(3.50%)	1.23
	19	4.0016	H-2→L(16.43%), H-5→L+1(7.54%), H-3→L+1(6.38%), H-4→L(5.58%), H-1→L+8(4.08%)	1.18
	20	4.0065	H-2→L+1(14.68%), H-5→L(6.65%), H-3→L(5.88%), H-4→L+1(5.05%), H-1→L+9(4.39%), H→L+2(3.63%), H-6→L(3.39%), H→L+1(3.10%)	0.65

[a] H: HOMO ; L: LUMO

[b] 1d: Degenerated orbital or 1st excited state.

Table S12 Component analysis of the excited-state **BrDBTCz** configurated as dimer 3

State	No.	Energy (eV)	Transition Contributions (%)[a]	ξ_{Tn-S1} (cm^{-1})
S_n	1	3.6563	H→L+3(83.77%), H→L+7(6.03%), H→L+1(3.16%)	--
	2	3.6921	H-1→L+1(72.99%), H-1→L+2(14.73%), H-1→L+4(7.39%)	
	3	3.7527	H→L(96.77%)	
	4	3.7606	H→L+2(60.74%), H→L+1(28.19%)	
	5	3.7839	H-1→L(92.15%)	
	6	3.8605	H→L+1(58.30%), H→L+2(34.38%)	
	7	3.9647	H-2→L+3(24.40%), H-4→L+2(11.44%), H→L+8(10.75%), H-2→L+2(10.28%), H-2→L(10.20%), H-2→L+1(9.14%), H-6→L+2(5.93%), H-4→L+1(3.63%)	
	8	3.9726	H-2→L(34.79%), H-2→L+3(20.63%), H→L+8(18.96%), H-2→L+2(5.64%), H-4→L+2(5.60%), H-6→L+2(3.41%)	
	9	3.9814	H-1→L+5(56.37%), H-3→L(10.31%), H-5→L(8.43%), H-7→L(7.75%)	
	10	3.9858	H-2→L(50.48%), H-2→L+3(23.53%), H→L+8(13.14%)	
T_n	1	3.1542	H-3→L+5(35.20%), H-3→L+6(28.56%), H-3→L+7(12.92%)	0.00
	1d[b]	3.1559	H-2→L+9(56.60%), H-2→L+8(16.97%), H→L+19(7.13%)	0.52
	3	3.3019	H-4→L+3(33.13%), H-4→L+7(6.44%), H-6→L+8(5.81%), H→L+8(4.89%), H-4→L+8(4.29%)	2.40
	4	3.3061	H-5→L+1(23.30%), H-5→L+4(7.73%), H-6→L+1(5.24%), H-5→L+2(5.24%), H-7→L+5(4.91%), H-1→L+5(4.71%), H-7→L+10(3.62%), H-7→L+6(3.52%), H-7→L(3.44%)	0.21
	5	3.3625	H→L+9(57.82%), H→L+8(23.79%)	1.12
	6	3.3652	H-1→L+5(46.14%), H-1→L+6(27.54%), H-1→L+7(12.18%)	0.02
	7	3.5022	H-4→L+12(13.82%), H-4→L+2(7.08%), H-8→L+13(5.45%), H-6→L+3(4.63%), H-8→L+8(4.37%), H-8→L+15(3.59%), H-8→L+12(3.57%), H-4→L+3(3.52%), H-6→L+13(3.49%), H-4→L+11(3.26%)	0.79
	8	3.5054	H-5→L+10(12.43%), H-5→L(6.99%), H-7→L+1(5.67%), H-10→L+10(4.29%), H-7→L+11(4.14%), H-10→L+11(4.00%), H-5→L+11(3.75%), H-10→L+5(3.56%), H-10→L+14(3.52%)	0.28
	9	3.5639	H-6→L+2(18.63%), H-17→L+2(13.85%), H-4→L+2(7.55%), H-12→L+2(6.43%), H-12→L+7(5.53%), H-6→L+1(4.23%), H-5→L+2(3.84%), H-12→L+3(3.71%), H-12→L+6(3.04%)	1.25
	10	3.5711	H-7→L(27.42%), H-20→L(17.59%), H-13→L+4(8.45%), H-13→L(8.20%), H-5→L(6.42%), H-13→L+1(3.58%)	0.08
	11	3.5949 (ΔE_{S1Tn}=0.0614)	H→L+3(70.05%), H→L+9(6.20%), H→L+7(4.86%), H-6→L+3(3.60%)	1.24
	12	3.6270	H-1→L+1(61.94%), H-1→L+2(12.80%), H-1→L+4(6.28%), H-1→L+6(5.32%)	0.02

State	No.	Energy (eV)	Transition Contributions (%)[a]	ξ_{Tn-S1} (cm^{-1})
T_n	13	3.7243 (ΔE_{S1Tn}=0.0680)	H→L+2(41.81%), H→L+1(19.77%), H-4→L+3(6.88%), H→L+8(6.37%), H→L+3(5.29%)	3.56
	14	3.7434	H-1→L(62.18%), H-1→L+5(4.72%), H-5→L+1(4.69%), H-1→L+6(3.14%)	0.13
	15	3.7527	H→L(98.76%)	2.61
	16	3.8297	H→L+2(29.51%), H-4→L+3(14.01%), H-4→L+8(8.80%), H-6→L+8(7.02%), H-2→L+3(4.35%), H→L+8(4.22%)	2.48
	17	3.8549	H-1→L(28.68%), H-5→L+1(9.52%), H-7→L+5(6.74%), H-5→L+5(6.39%), H-7→L+6(4.87%), H-3→L+1(3.37%), H-1→L+5(3.11%)	0.93
	18	3.8624	H→L+1(66.66%), H→L+2(22.85%)	3.11
	19	3.9518	H→L+8(16.94%), H-4→L+2(10.81%), H-6→L+3(10.37%), H-2→L+2(9.22%), H→L+9(7.61%), H→L+1(3.99%), H-2→L+1(3.90%)	2.65
	20	3.9597	H-2→L+3(23.93%), H-6→L+3(23.61%), H-4→L+8(6.44%), H-5→L+3(6.17%), H-2→L(5.60%), H→L+8(3.84%), H-2→L+1(3.43%)	2.63

[a] H: HOMO ; L: LUMO

[b] 1d: Degenerated orbital or 1st excited state.

Table S13 Component analysis of the excited-state **BrDBTCz** configurated as dimer 4

State	No.	Energy (eV)	Transition Contributions (%)[a]	ξ_{Tn-S1} (cm^{-1})
S_n	1	3.7691	H→L+2(46.16%), H-1→L+3(42.47%)	--
	1d[b]	3.7709	H-1→L+2(45.09%), H→L+3(42.95%)	
	3	3.8843	H-1→L(44.76%), H→L+1(38.74%), H→L(3.86%)	
	4	3.8846	H-1→L+1(41.35%), H→L(38.12%), H→L+1(7.39%)	
	5	3.9909	H→L(29.37%), H-1→L+1(20.87%), H-1→L+5(19.02%), H→L+4(15.09%), H→L+7(5.46%)	
	6	3.9911	H-1→L(26.82%), H→L+1(21.10%), H→L+5(19.10%), H-1→L+4(15.89%), H-1→L+7(5.26%), H-1→L+1(3.12%)	
	7	4.0114	H→L(18.79%), H-1→L+5(12.15%), H-1→L(10.85%), H→L+5(10.45%), H-1→L+1(10.38%), H→L+4(9.62%), H→L+1(6.87%), H-1→L+4(4.94%), H→L+7(4.50%)	
	8	4.0115	H→L+1(19.06%), H-1→L+1(17.05%), H-1→L+4(11.50%), H→L+5(11.38%), H-1→L(8.98%), H-1→L+5(8.24%), H→L+4(5.51%), H-1→L+7(4.15%), H→L(3.40%)	
	9	4.0281	H-4→L(19.27%), H-5→L+1(18.56%), H-7→L(12.30%), H-6→L+1(12.24%), H-2→L+1(6.70%), H-3→L(5.97%), H→L+9(5.37%), H-1→L+8(5.09%)	
	10	4.0326	H-4→L+1(18.64%), H-5→L(17.73%), H-7→L+1(13.30%), H-6→L(12.82%), H-2→L(6.82%), H-3→L+1(5.73%), H-1→L+9(4.87%), H→L+8(4.48%)	
T_n	1	3.1567	H-2→L+4(16.26%), H-2→L+5(14.03%), H-3→L+4(13.93%), H-3→L+5(12.00%), H-2→L+7(3.35%)	0.28
	1d[b]	3.1573	H-3→L+5(16.40%), H-3→L+4(14.10%), H-2→L+5(13.74%), H-2→L+4(11.82%), H-3→L+7(3.84%), H-2→L+7(3.22%)	0.35
	3	3.3046	H-4→L+2(9.54%), H-5→L+2(9.31%), H-5→L+3(8.62%), H-4→L+3(8.41%), H-7→L+9(3.07%)	1.40
	4	3.3048	H-4→L+3(9.85%), H-5→L+3(9.23%), H-4→L+2(8.45%), H-5→L+2(8.32%)	1.16
	5	3.3484	H-1→L+4(21.23%), H-1→L+5(16.68%), H→L+4(16.05%), H→L+5(14.10%), H-1→L+7(3.98%), H-1→L+6(3.78%), H→L+6(3.17%)	0.60
	6	3.3487	H→L+5(19.52%), H→L+4(18.42%), H-1→L+5(16.28%), H-1→L+4(13.75%), H→L+7(4.56%), H-1→L+7(3.43%), H→L+6(3.25%)	0.73
	7	3.5070	H-5→L+11(5.67%), H-4→L+10(5.45%), H-4→L+11(4.15%), H-5→L+10(3.59%), H-4→L(3.12%)	0.51
	8	3.5070	H-4→L+11(5.59%), H-5→L+10(5.54%), H-4→L+10(3.90%), H-5→L+11(3.84%), H-4→L+1(3.06%)	0.77

State	No.	Energy (eV)	Transition Contributions (%)[a]	ξ_{Tn-S1} (cm^{-1})
T_n	9	3.5751	H-6→L(11.75%), H-7→L(6.91%), H-16→L(5.52%), H-17→L(4.94%), H-6→L+1(4.85%), H-7→L+1(3.38%), H-5→L(3.02%)	0.80
	10	3.5753	H-7→L+1(11.33%), H-6→L+1(7.40%), H-17→L+1(6.10%), H-7→L(5.27%), H-16→L+1(4.33%), H-5→L+1(3.11%)	1.03
	11	3.6880 (ΔE_{S1Tn}=0.0811)	H→L+2(20.56%), H→L+3(18.39%), H-1→L+2(15.90%), H-1→L+3(14.74%)	1.22
	12	3.6882 (ΔE_{S1Tn}=0.0809)	H-1→L+3(20.42%), H-1→L+2(18.16%), H→L+3(16.65%), H→L+2(14.29%)	1.00
	13	3.7988 (ΔE_{S1Tn}=0.0297)	H→L+1(9.35%), H-1→L+1(6.66%), H-5→L+2(4.45%), H-4→L+2(4.09%), H-4→L+3(3.86%), H→L(3.71%), H-5→L+3(3.44%), H-1→L(3.28%), H→L+2(3.18%)	3.53
	14	3.7989 (ΔE_{S1Tn}=0.0298)	H-1→L(8.49%), H→L(7.52%), H-5→L+3(4.18%), H-4→L+2(4.11%), H-1→L+1(4.11%), H-4→L+3(4.01%), H-5→L+2(3.52%), H-1→L+3(3.08%)	2.83
	15	3.9023	H→L(23.16%), H-1→L(18.23%), H-1→L+1(14.56%), H→L+1(3.99%), H-5→L+8(3.68%), H-6→L+8(3.43%), H-4→L+9(3.26%)	1.38
	16	3.9023	H→L+1(27.39%), H-1→L+1(13.48%), H-1→L(13.04%), H→L(6.07%), H-5→L+9(3.67%), H-4→L+8(3.28%)	2.38
	17	3.9803	H-7→L+2(22.43%), H-6→L+3(15.52%), H-7→L+3(9.18%), H-6→L+2(5.08%)	2.27
	18	3.9804	H-6→L+2(20.71%), H-7→L+3(16.52%), H-6→L+3(10.80%), H-7→L+2(4.07%)	3.04
	19	4.0005	H-1→L(34.03%), H→L(28.01%), H→L+1(26.06%), H-1→L+1(5.40%)	0.17
	20	4.0009	H-1→L+1(42.61%), H→L(22.34%), H→L+1(21.28%), H-1→L(7.47%)	0.18

[a] H: HOMO ; L: LUMO

[b] 1d: Degenerated orbital or 1st excited state.

Table S14 Component analysis of the excited-state **BrDBTCz** configurated as dimer 5

State	No.	Energy (eV)	Transition Contributions (%)[a]	ξ_{Tn-S1} (cm^{-1})
S_n	1	3.6905	H-1→L(47.39%), H→L+1(29.94%), H→L+3(10.99%), H-1→L+2(6.18%)	--
	1d[b]	3.6909	H→L(47.94%), H-1→L+1(29.38%), H-1→L+3(11.03%), H→L+2(6.14%)	
	3	3.9086	H-1→L+1(18.25%), H→L(15.02%), H→L+1(14.92%), H-1→L+3(6.79%), H-1→L(6.14%), H→L+3(5.88%), H→L+4(5.88%), H→L+2(4.63%), H-1→L+7(3.02%)	
	4	3.9089	H→L+1(18.50%), H-1→L+1(15.02%), H-1→L(14.88%), H→L+3(7.33%), H→L(6.04%), H-1→L+4(5.85%), H-1→L+3(5.62%), H-1→L+2(4.31%)	
	5	3.9936	H-3→L(34.99%), H-2→L+1(23.67%), H-2→L+3(7.94%), H-2→L(7.88%), H-4→L(4.53%)	
	6	3.9943	H-2→L(33.36%), H-3→L+1(22.61%), H-3→L(7.82%), H-3→L+3(7.62%), H-1→L+5(5.76%), H→L+4(4.06%), H-5→L(3.31%)	
	7	4.0110	H→L+5(35.01%), H-1→L+4(30.94%), H→L+1(10.16%), H-1→L+6(5.05%), H-1→L(4.31%)	
	8	4.0137	H-1→L+5(30.56%), H→L+4(29.43%), H-1→L+1(10.74%), H→L(5.37%), H-3→L+1(4.48%), H→L+6(3.21%)	
	9	4.0337	H→L+2(38.68%), H-1→L+3(34.26%), H→L(13.49%), H-1→L+1(4.06%), H→L+6(3.50%)	
	10	4.0351	H-1→L+2(38.60%), H→L+3(35.55%), H-1→L(15.48%)	
T_n	1	3.1520	H-2→L+5(21.06%), H-2→L+6(15.64%), H-3→L+5(10.08%), H-2→L+4(9.96%), H-3→L+6(7.47%), H-3→L+4(4.76%), H-2→L+7(4.15%)	0.32
	1d[b]	3.1528	H-3→L+5(21.13%), H-3→L+6(16.07%), H-2→L+5(10.11%), H-3→L+4(9.41%), H-2→L+6(7.68%), H-2→L+4(4.49%), H-3→L+7(4.19%)	0.30
	3	3.2888	H-4→L(15.31%), H-5→L+3(14.79%), H-5→L+1(4.64%), H-4→L+4(3.36%), H-6→L+3(3.18%)	1.79
	4	3.2889	H-5→L(15.05%), H-4→L+3(15.03%), H-4→L+1(4.64%), H-5→L+4(3.26%), H-7→L+3(3.04%), H-6→L+4(3.02%)	0.60
	5	3.3623	H-1→L+5(23.32%), H→L+5(14.66%), H-1→L+6(13.23%), H→L+6(10.83%), H-1→L+4(10.53%), H→L+4(8.54%)	0.62
	6	3.3625	H→L+5(23.43%), H-1→L+5(14.73%), H→L+6(13.68%), H-1→L+6(11.11%), H→L+4(9.93%), H-1→L+4(8.14%)	0.59
	7	3.5096	H-5→L+10(4.68%), H-4→L+10(4.52%), H-4→L+11(4.17%), H-5→L+11(3.91%)	0.74
	8	3.5098	H-4→L+10(4.68%), H-5→L+10(4.51%), H-5→L+11(4.19%),	0.82

State	No.	Energy (eV)	Transition Contributions (%)[a]	ξ_{Tn-S1} (cm^{-1})
			H-4→L+11(3.93%)	
T_n	9	3.5933	H-6→L+1(12.44%), H-7→L+2(8.06%), H-13→L+9(7.40%), H-16→L(6.85%), H-5→L+1(4.85%), H-12→L+8(4.84%), H-17→L+1(4.33%), H-12→L+2(4.27%), H-16→L+2(3.48%), H-17→L+3(3.47%)	0.71
	10	3.5957	H-7→L+1(11.53%), H-6→L+2(10.01%), H-13→L+8(6.26%), H-17→L(5.76%), H-12→L+9(5.71%), H-13→L+2(5.08%), H-16→L+1(5.04%), H-4→L+1(4.73%), H-16→L+3(3.99%), H-5→L+2(3.36%), H-17→L+2(3.08%)	0.02
	11	3.6241 (ΔE_{S1Tn}=0.0664)	H→L(33.21%), H-1→L+1(27.08%), H-1→L+3(8.50%), H→L+2(6.91%), H-1→L+7(4.08%)	0.22
	12	3.6243 (ΔE_{S1Tn}=0.0662)	H-1→L(32.29%), H→L+1(27.48%), H→L+3(8.73%), H-1→L+2(6.95%), H→L+7(4.16%)	1.28
	13	3.7600 (ΔE_{S1Tn}=0.0695)	H-1→L(11.18%), H-4→L(9.15%), H→L+3(7.61%), H-5→L+1(7.17%), H-6→L+7(4.71%), H-1→L+4(4.36%), H-6→L+1(4.23%), H-5→L+7(4.17%), H→L+7(3.17%)	4.11
	14	3.7618 (ΔE_{S1Tn}=0.0713)	H→L(10.59%), H-5→L(8.99%), H-1→L+3(7.69%), H-4→L+1(7.26%), H-7→L+7(4.71%), H→L+4(4.63%), H-4→L+7(4.39%), H-7→L+1(3.83%), H-1→L+7(3.04%)	0.56
	15	3.9061	H→L+1(19.56%), H-1→L(12.47%), H→L+3(7.76%), H→L(4.37%), H-5→L+7(3.62%), H-1→L+2(3.42%), H-1→L+1(3.01%), H-4→L+4(3.00%)	1.67
	16	3.9065	H-1→L+1(20.22%), H→L(12.37%), H-1→L+3(7.69%), H-1→L(4.32%), H-4→L+7(3.67%), H→L+2(3.60%), H-1→L+7(3.01%)	0.94
	17	3.9318	H-7→L(26.14%), H-6→L+1(16.14%), H-6→L+3(12.76%), H-7→L+2(6.19%), H→L+1(3.79%)	3.42
	18	3.9319	H-6→L(27.51%), H-7→L+1(15.11%), H-7→L+3(13.21%), H-6→L+2(5.89%), H-1→L+1(4.02%)	0.16
	19	4.0052	H-2→L(26.14%), H-2→L+1(13.93%), H-3→L(10.44%), H-3→L+1(8.40%), H-2→L+3(4.01%)	0.43
	20	4.0055	H-3→L(26.35%), H-3→L+1(14.28%), H-2→L(9.80%), H-2→L+1(8.15%), H-3→L+3(3.90%)	0.39

[a] H: HOMO ; L: LUMO

[b] 1d: Degenerated orbital or 1st excited state.

Table S15 Component analysis of the excited-state **BrDBTCz** configurated as dimer 6

State	No.	Energy (eV)	Transition Contributions (%)[a]	ξ_{Tn-S1} (cm^{-1})
S_n	1	3.7030	H→L+2(45.79%), H-1→L+3(42.45%), H→L+4(3.62%)	--
	1d[b]	3.7046	H-1→L+2(44.71%), H→L+3(43.67%), H-1→L+4(3.61%)	
	3	3.8025	H→L(50.52%), H-1→L+1(39.68%)	
	4	3.8032	H→L+1(48.67%), H-1→L(41.35%)	
	5	3.8512	H-1→L(46.18%), H→L+1(34.56%), H→L(11.54%), H-1→L+1(6.96%)	
	6	3.8514	H-1→L+1(47.18%), H→L(33.41%), H→L+1(12.21%), H-1→L(6.42%)	
	7	3.9810	H→L+3(38.39%), H-1→L+2(28.34%), H-1→L+6(12.25%), H→L+7(9.17%)	
	8	3.9812	H-1→L+3(42.39%), H→L+2(31.33%), H→L+6(9.74%), H-1→L+7(6.73%)	
	9	3.9906	H-1→L+6(23.97%), H→L+7(20.12%), H-1→L+2(19.44%), H→L+3(10.30%), H-2→L+1(3.76%), H-4→L(3.18%), H-5→L+1(3.10%)	
	10	3.9916	H→L+6(26.66%), H-1→L+7(21.40%), H→L+2(13.31%), H-1→L+3(6.04%), H-2→L(5.58%), H-4→L+1(4.07%), H-5→L(3.88%)	
T_n	1	3.1535	H-2→L+6(17.23%), H-3→L+8(16.36%), H-3→L+7(13.30%), H-2→L+9(12.62%), H-3→L+6(4.57%), H-2→L+8(4.45%), H-2→L+7(3.57%), H-3→L+9(3.29%)	0.41
	1d[b]	3.1537	H-3→L+6(16.73%), H-2→L+8(16.67%), H-2→L+7(13.70%), H-3→L+9(12.43%), H-2→L+6(4.57%), H-3→L+8(4.27%), H-3→L+7(3.56%), H-2→L+9(3.46%)	0.17
	3	3.3105	H-4→L+3(10.93%), H-5→L+2(10.56%), H-4→L+2(7.18%), H-5→L+3(6.54%), H-4→L+5(3.27%)	1.24
	4	3.3105	H-5→L+3(10.78%), H-4→L+2(10.74%), H-5→L+2(6.99%), H-4→L+3(6.75%), H-5→L+5(3.09%)	0.99
	5	3.3659	H→L+6(21.14%), H-1→L+7(16.70%), H-1→L+8(15.26%), H→L+9(11.17%), H-1→L+6(6.24%), H→L+7(5.26%), H→L+8(4.87%), H-1→L+9(3.24%)	1.02
	6	3.3662	H-1→L+6(20.58%), H→L+7(17.17%), H→L+8(15.53%), H-1→L+9(11.03%), H→L+6(6.24%), H-1→L+7(5.26%), H-1→L+8(4.69%), H→L+9(3.40%)	0.51
	7	3.5083	H-4→L+10(8.98%), H-5→L+11(8.67%), H-4→L+1(4.16%), H-5→L(3.91%), H-7→L+2(3.69%), H-6→L+3(3.68%)	0.57
	8	3.5083	H-4→L+11(8.87%), H-5→L+10(8.78%), H-4→L(4.16%), H-5→L+1(3.95%), H-7→L+3(3.72%), H-6→L+2(3.66%)	0.58
	9	3.5732	H-7→L(7.81%), H-6→L(7.61%), H-6→L+1(5.69%), H-18→L(5.64%), H-7→L+1(5.26%), H-19→L(4.77%), H-18→L+1(3.76%), H-19→L+1(3.54%)	0.62

State	No.	Energy (eV)	Transition Contributions (%)[a]	ξ_{Tn-S1} (cm^{-1})
T_n	10	3.5733	H-7→L+1(7.90%), H-6→L+1(7.57%), H-6→L(5.62%), H-7→L(5.29%), H-18→L+1(5.18%), H-19→L+1(5.16%), H-19→L(3.88%), H-18→L(3.50%)	0.58
	11	3.6368 (ΔE_{S1Tn}=0.0662)	H→L+3(19.82%), H-1→L+2(18.91%), H→L+2(18.59%), H-1→L+3(17.80%)	0.78
	12	3.6369 (ΔE_{S1Tn}=0.0661)	H-1→L+3(19.37%), H→L+2(19.36%), H→L+3(18.47%), H-1→L+2(17.94%)	0.76
	13	3.7578	H→L(25.85%), H-1→L+1(18.46%), H-1→L(8.50%), H→L+1(4.95%), H-5→L+2(3.19%), H-4→L+3(3.18%)	4.28
	14	3.7580	H→L+1(24.79%), H-1→L(19.42%), H-1→L+1(8.49%), H→L(5.04%), H-4→L+2(3.23%), H-5→L+3(3.15%)	2.33
	15	3.8511	H→L(45.37%), H-1→L+1(33.18%), H-1→L(13.33%), H→L+1(6.56%)	0.29
	16	3.8512	H→L+1(43.62%), H-1→L(35.74%), H-1→L+1(12.29%), H→L(7.31%)	0.21
	17	3.8652	H-1→L(16.11%), H→L+1(11.93%), H-4→L+2(5.97%), H-5→L+3(5.58%), H-5→L+7(3.63%), H-6→L+9(3.59%)	1.43
	18	3.8654	H-1→L+1(20.21%), H→L(8.59%), H-5→L+2(5.79%), H-4→L+3(5.59%), H-4→L+7(3.56%), H-7→L+9(3.51%), H-5→L+9(3.03%)	2.50
	19	3.9734	H-2→L(7.66%), H→L+9(7.60%), H-1→L+8(7.24%), H-5→L(7.01%), H-4→L+1(6.92%), H-6→L+3(5.32%), H-7→L+2(5.27%), H→L+2(5.00%), H-1→L+7(4.58%), H→L+6(4.29%), H-3→L+1(3.72%), H-1→L+3(3.18%)	1.62
	20	3.9738	H-1→L+9(7.85%), H→L+8(7.75%), H-2→L+1(7.41%), H-5→L+1(7.35%), H-4→L(7.16%), H-7→L+3(4.77%), H-6→L+2(4.77%), H→L+7(4.74%), H-1→L+6(4.38%), H-3→L(4.12%), H-1→L+2(4.12%)	0.09

[a] H: HOMO ; L: LUMO

[b] 1d: Degenerated orbital or 1st excited state.

8. High Performance Liquid Chromatography (HPLC)

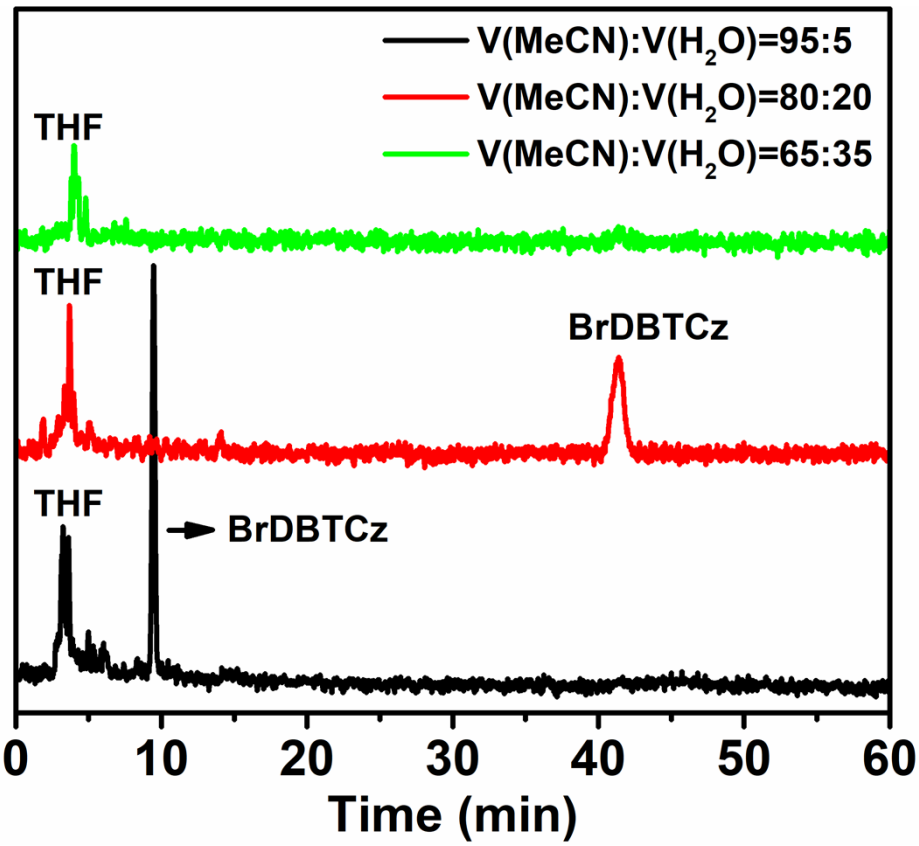


Figure S10 The HPLC spectra of the THF-dissolved **BrDBTCz** monitored at 346 nm with the acetonitrile-water mixed eluent. Generally, 5 mg of **BrDBTCz** was dissolved in 5 mL of THF, 10 uL of the solution was then added into the 1 mL of eluent with certain ratio.