Supplementary information for

Heteroatom effects on the magnetic exchange interactions in bis(2,4,6-trichlorophenyl)methyl-based diradicals

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Table S1. Energies in a.u., $<S^2>$, $\Delta E_{S\text{-}T}$ (kcal mol^{-1}) intramolecular magnetic exchange coupling constant (J, cm^{-1}) for BTM-based diradicals calculated at the theoretical level of (U)M06-2X/def2-SVP.

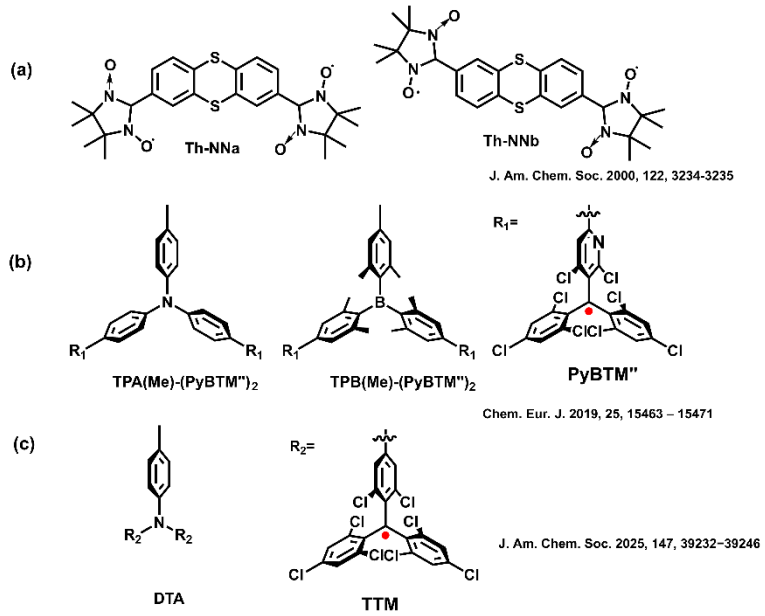
Diradicals	$E_{BS}(<S^2>)$	$E_T(<S^2>)$	$\Delta E_{S\text{-}T}$	*J*
BTMa	-7052.679759(1.040)	-7052.683016(2.104)	4.04	672.04
BTMaN1	-7084.722465(1.038)	-7084.725227(2.100)	3.43	571.05
BTMaB	-7026.197095(1.045)	-7026.195704(2.053)	-1.78	-303.01
BTMaC	-7053.879549(1.042)	-7053.879617(2.043)	0.09	14.90
BTMaN2	-7085.945850(0.917)	-7085.940776(2.046)	-5.77	-986.72
BTMaO	-7125.608560(1.039)	-7125.607636(2.045)	-1.18	-201.51
BTMaBN	-7056.091686(1.030)	-7056.090688(2.037)	-1.27	-217.44
BTMaNB	-7056.094829(1.016)	-7056.093136(2.037)	-2.12	-363.95
BTMb	-7052.687422(0.786)	-7052.678569(2.037)	-9.05	-1553.44
BTMbN1	-7084.729816(0.783)	-7084.721160(2.038)	-8.82	-1513.86
BTMbB	-7026.196060(1.054)	-7026.196718(2.067)	0.84	142.56
BTMbC	-7053.879780(1.043)	-7053.879738(2.042)	-0.05	-9.23
BTMbN2	-7085.942762(1.030)	-7085.944166(2.071)	1.75	295.84
BTMbO	-7125.607918(1.046)	-7125.608449(2.054)	0.68	115.57
BTMbBN	-7056.092625(1.028)	-7056.092758(2.045)	0.17	28.62

Table S2 Evaluation of the effect of basis set on the calculated results

Diradical	Basis set	Energy (a.u.) ($<S^2>$)		J/cm^{-1}
		BS	T	
BTM3a	def2-SVP	-7049.856971 (1.056)	-7049.861663 (2.167)	926.44
	def2-TZVP	-7053.349298 (1.053)	-7053.353836 (2.154)	904.80
	6-311+G(d,p)	-7053.132063 (1.053)	-7053.136542 (2.154)	892.89
BTM3b	def2-SVP	-7049.864868 (0.916)	-7049.85581 (2.055)	-1746.37
	def2-TZVP	-7053.357560 (0.859)	-7053.348054 (2.052)	-1748.02
	6-311+G(d,p)	-7053.140059 (0.871)	-7053.130796 (2.052)	-1720.55
TTM3a	def2-SVP	-8887.063567 (1.053)	-8887.064863 (2.119)	266.81
	def2-TZVP	-8891.185867 (1.051)	-8891.187122 (2.111)	259.89
	6-311+G(d,p)	-8890.954833 (1.051)	-8890.956097 (2.112)	261.73
TTM3b	def2-SVP	-8887.065475 (1.092)	-8887.06346 (2.052)	-460.37
	def2-TZVP	-8891.187895 (1.081)	-8891.185855 (2.051)	-461.46
	6-311+G(d,p)	-8890.957509 (1.081)	-8890.95546 (2.051)	-464.02

Table S3 The calculated *J* values (cm^{-1}) for some heteroatom-mediated diradicals with different functionals in combination with def2-SVP basis set.

	Th-NNa	Th-NNb	TPA(Me)-(PyBTM'')$_2$	TPB(Me)-(PyBTM'')$_2$
UB3LYP	-1.76	0.88	-12.62	-0.13
UPBE0	-1.11	0.44	-12.02	-0.02
UM06-2X	0.22	-0.44	-1.89	0.15
UCAM-B3LYP	0	-0.44	-5.27	0.04
UωB97XD	0.66	-0.66	-4.22	-6.31
Exp	-0.97	3.82	-5.65	-8.10



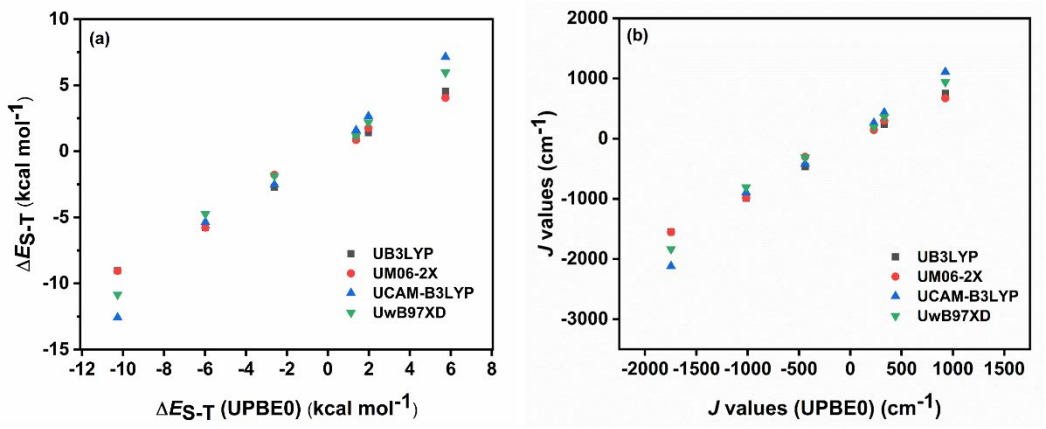


Fig. S1 Comparisons of the calculated $\Delta E_{S\text{-}T}$ (kcal·mol^{-1}) (a) and J values (cm^{-1}) (b) between the functional PBE0 and other functionals in combination with def2-SVP basis set.

Table S4 Comparisons of $\Delta E_{S\text{-}T}$ (kcal • mol^{-1}) and J values (cm^{-1}) (in parentheses) calculated by different functionals in combination with def2-SVP basis set.

Diradical	UB3LYP	UPBE0	UM06-2X	UCAM-B3LYP	UωB97XD
BTMa	4.516 (741.93)	5.740 (926.44)	4.042 (672.04)	7.134 (1107.69)	5.959 (938.87)
BTMaB	-2.726 (-465.03)	-2.610 (-440.21)	-1.778 (-303.01)	-2.525 (-419.43)	-1.858 (-311.01)
BTMaN2	-5.775 (-988.29)	-5.977 (-1014.39)	-5.772 (-986.72)	-5.359 (-895.23)	-4.745 (-809.40)
BTMb	-9.038 (-1550.15)	-10.260 (-1746.37)	-9.047 (-1553.44)	-12.571 (--2119.08)	-10.849 (-1836.54)
BTMbB	1.196 (202.42)	1.379 (230.15)	0.842 (142.56)	1.591 (259.77)	1.146 (189.37)
BTMbN2	1.409 (238.86)	1.979 (331.38)	1.752 (295.84)	2.649 (432.36)	2.177 (358.39)

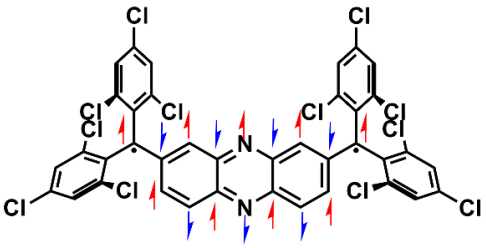
Table S5 Energies in a.u., $<S^2>$, $\Delta E_{S\text{-}T}$ (kcal mol^{-1}) and intramolecular magnetic exchange coupling constant (J, cm^{-1}) for TTM-based diradicals calculated at the theoretical level of (U)PBE0/def2-SVP

Diradicals	$E_{BS}(<S^2>)$	$E_T(<S^2>)$	$\Delta E_{S\text{-}T}$	J
BTMa	-7049.856971(1.056)	-7049.861663(2.167)	5.74	926.44
BTMaN1	-7081.878416(1.051)	-7081.882326(2.154)	4.79	778.05
BTMaB	-7023.375153(1.051)	-7023.373101(2.074)	-2.61	-440.21
BTMaC	-7051.058637(1.070)	-7051.058743(2.073)	0.14	23.21
BTMaN2	-7083.106996(0.912)	-7083.101687(2.061)	-5.98	-1014.39
BTMaO	-7122.740198(1.051)	-7122.738847(2.067)	-1.72	-291.69
BTMaBN	-7053.261282(1.038)	-7053.260111(2.058)	-1.48	-251.99
BTMaNB	-7053.264077(1.022)	-7053.262483(2.057)	-1.99	-337.86
BTMb	-7049.864868(0.916)	-7049.855810(2.055)	-10.26	-1746.37
BTMbN1	-7081.885894(0.901)	-7081.877092(2.056)	-9.83	-1672.11
BTMbB	-7023.373425(1.074)	-7023.374497(2.096)	1.38	230.15
BTMbC	-7051.058901(1.073)	-7051.058833(2.071)	-0.09	-14.95
BTMbN2	-7083.103579(1.031)	-7083.105177(2.089)	1.98	331.38
BTMbO	-7122.739139(1.067)	-7122.739910(2.081)	0.99	166.94
BTMbBN	-7053.262047(1.038)	-7053.262068(2.066)	0.03	4.48
TTMa	-8887.063567(1.053)	-8887.064863(2.119)	1.62	266.81
TTMaN1	-8919.079493(1.053)	-8919.080634(2.108)	1.43	237.27
TTMaB	-8860.579231(1.056)	-8860.578841(2.054)	-0.50	-85.74
TTMaC	-8888.268968(1.055)	-8888.268993(2.056)	0.03	5.48
TTMaN2	-8920.312332(1.044)	-8920.310927(2.056)	-1.79	-304.93
TTMaO	-8959.937282(1.057)	-8959.937008(2.055)	-0.35	-60.24
TTMaBN	-8890.472905(1.050)	-8890.47261(2.052)	-0.38	-64.62
TTMaNB	-8890.468821(1.050)	-8890.468613(2.052)	-0.27	-45.57
TTMb	-8887.065475(1.092)	-8887.06346(2.052)	-2.70	-460.37
TTMbN1	-8919.081229(1.076)	-8919.07923(2.053)	-2.64	-449.04
TTMbB	-8860.579777(1.055)	-8860.579989(2.062)	0.27	46.18
TTMbC	-8888.269354(1.055)	-8888.269307(2.055)	-0.06	-10.32
TTMbN2	-8920.312308(1.048)	-8920.312838(2.076)	0.67	113.20
TTMbO	-8959.937429(1.055)	-8959.937624(2.061)	0.25	42.56
TTMbBN	-8890.471362(1.050)	-8890.471407(2.055)	0.06	9.83

Table S6 Bond length (Å) of the covalent bonds connecting the BTM moieties and the couplers

Diradicals	BS	T	φ(°)*	Diradicals	BS	T	φ(°)*
BTMa	1.438	1.426		**TTMa**	1.468	1.461	
BTMaN1	1.438	1.428		**TTMaN1**	1.467	1.461	
BTMaB	1.433	1.440		**TTMaB**	1.468	1.470	
BTMaC	1.442	1.442	35.6	**TTMaC**	1.470	1.470	26.4
BTMaN2	1.420	1.435		**TTMaN2**	1.453	1.460	
BTMaO	1.436	1.440		**TTMaO**	1.465	1.466	
BTMaBN	1.442	1.446		**TTMaBN**	1.469	1.470	
BTMaNB	1.436	1.442		**TTMaNB**	1.469	1.470	
BTMb	1.415	1.442		**TTMb**	1.458	1.469	
BTMbN1	1.415	1.443		**TTMbN1**	1.457	1.468	
BTMbB	1.438	1.435		**TTMaB**	1.470	1.469	
BTMbC	1.442	1.442	36.2	**TTMaC**	1.469	1.469	26.2
BTMbN2	1.430	1.427		**TTMbN2**	1.457	1.455	
BTMbO	1.439	1.437		**TTMbO**	1.466	1.465	
BTMbBN	1.439	1.439		**TTMbBN**	1.469	1.469	

*The angles between two planes are defined by the outer benzene rings of the couplers



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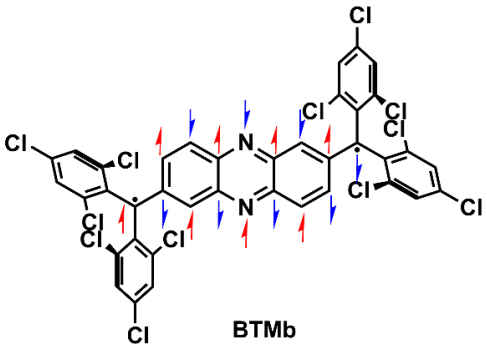

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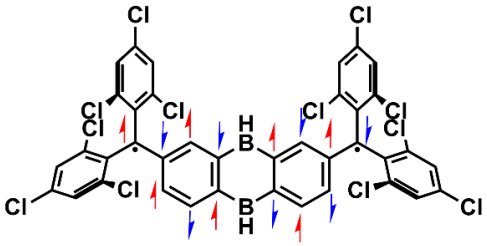

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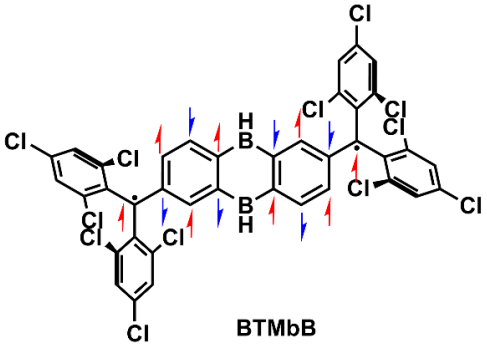

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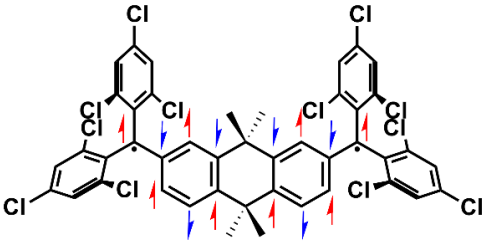

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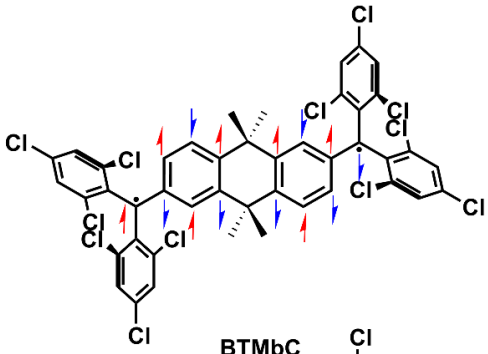

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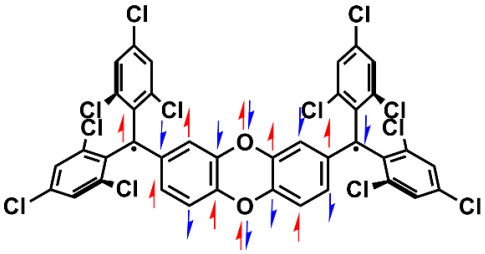

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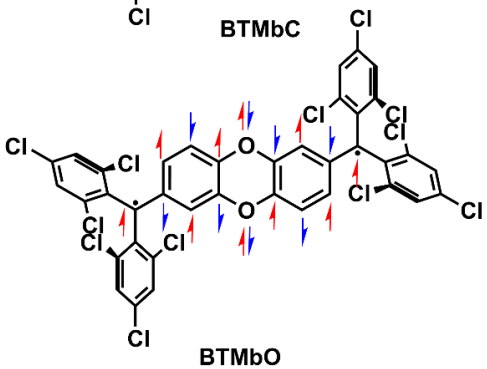

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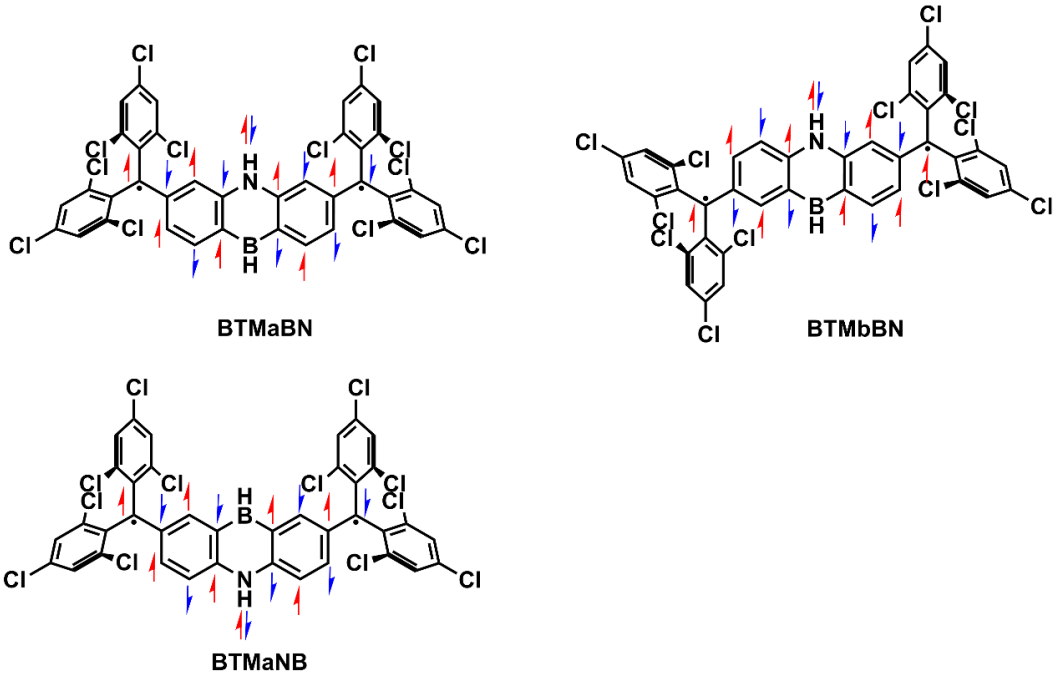

Fig. S2 Spin alternation patterns in BTMa and BTMb derivatives in this work. (The blue and red arrows indicate α-spin and β-spin, respectively).

Table S7 The Hirshfeld atomic spin density in the T state for BTM- and TTM-based diradicals*

Diradical	$C_{a(a')}$	X_1	X_2	Diradical	$C_{a(a')}$	X_1	X_2
BTMa	0.404	0.208	-0.096	**TTMa**	0.472	0.116	-0.070
BTMaN1	0.414	0.182	-0.084	**TTMaN1**	0.472	0.097	-0.058
BTMaB	0.444	-0.023	0.088	**TTMaB**	0.493	-0.010	0.039
BTMaC	0.452	-0.004	0.016	**TTMaC**	0.496	-0.002	0.007
BTMaN2	0.407	-0.002	0.108	**TTMaN2**	0.463	-0.002	0.057
BTMaO	0.443	-0.015	0.069	**TTMaO**	0.487	-0.008	0.032
BTMaBN	0.462	0.005	0.038	**TTMaBN**	0.494	0.002	0.019
BTMaNB	0.445	0.018	0.039	**TTMaNB**	0.493	0.009	0.016
BTMb	0.443	0.044	0.044	**TTMb**	0.489	0.019	0.019
BTMbN1	0.449	0.040	0.040	**TTMbN1**	0.488	0.018	0.018
BTMbB	0.433	0.040	0.040	**TTMbB**	0.490	0.013	0.013
BTMbC	0.452	0.006	0.006	**TTMbC**	0.496	0.003	0.003
BTMbN2	0.381	0.073	0.073	**TTMbN2**	0.448	0.038	0.038
BTMbO	0.434	0.033	0.033	**TTMbO**	0.484	0.014	0.014
BTMbBN	0.458	0.032	0.025	**TTMbBN**	0.490	0.008	0.017

* The atomic sites $C_{a(a')}$, X1 and X2 were shown in Figure 2.

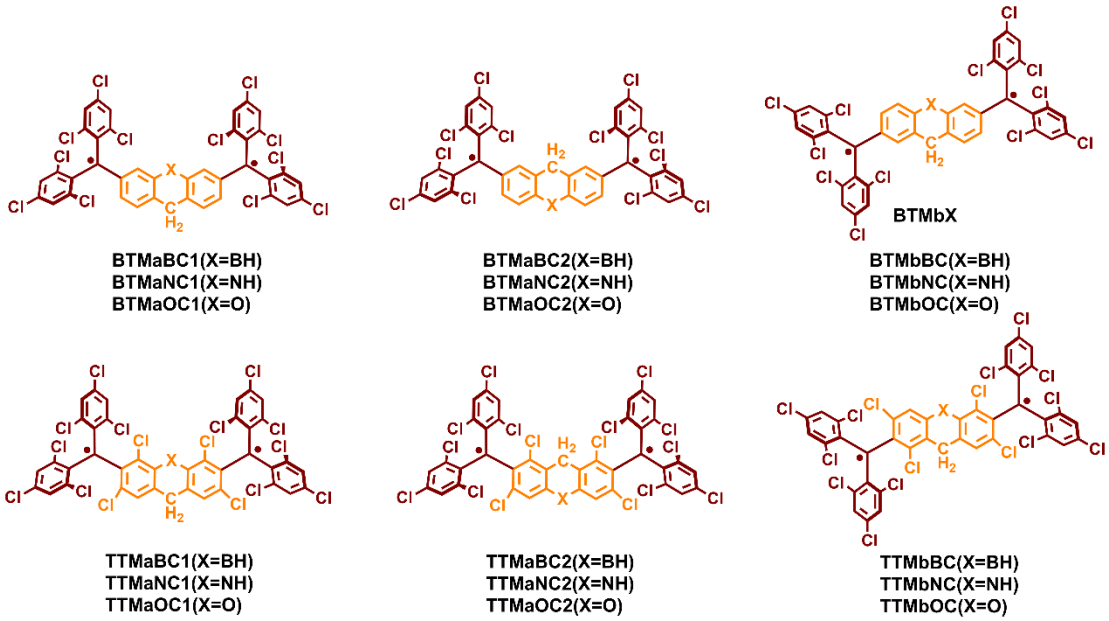

Figure S3. Molecular structures of mono-heteroatom doped BTM and TTM-based diradicals.

Table S8 Energies in a.u., $<S^2>$, $\Delta E_{S\text{-}T}$ (kcal mol^{-1}) and intramolecular magnetic exchange coupling constant (J, cm^{-1}) for mono-heteroatom doped BTM and TTM-based diradicals calculated at the theoretical level of (U)PBE0/def2-SVP

Diradicals	E_{BS}(<S^2>)	E_T(<S^2>)	$\Delta E_{S\text{-}T}$	J
BTMaBC1	-7037.219363(1.073)	-7037.219281(2.070)	-0.11	-18.05
BTMaBC2	-7037.221673(1.039)	-7037.220087(2.066)	-2.00	-338.92
BTMaNC1	-7067.081135(1.076)	-7067.080994(2.069)	-0.18	-31.16
BTMaNC2	-7067.088074(0.981)	-7067.084925(2.059)	-3.77	-640.76
BTMaOC1	-7086.902093(1.073)	-7086.902035(2.070)	-0.08	-12.77
BTMaOC2	-7122.740198(1.051)	-7122.738847(2.067)	-1.72	-291.70
BTMbBC	-7037.219932(1.063)	-7037.220175(2.075)	0.31	52.70
BTMbNC	-7083.103579(1.031)	-7083.105177(2.089)	1.05	177.69
BTMbOC	-7122.739139(1.067)	-7122.73991(2.081)	0.40	67.17
TTMaBC1	-8874.426586(1.054)	-8874.426581(2.053)	-0.01	-1.10
TTMaBC2	-8874.432042(1.052)	-8874.431663(2.054)	-0.49	-83.01
TTMaNC1	-8904.293524(1.058)	-8904.293474(2.056)	-0.06	-11.00
TTMaNC2	-8904.295549(1.048)	-8904.294875(2.053)	-0.86	-147.22
TTMaOC1	-8924.103701(1.057)	-8924.103685(2.055)	-0.02	-3.52
TTMaOC2	-8924.11368(1.048)	-8924.113467(2.054)	-0.27	-46.46
TTMbBC	-8874.429785(1.053)	-8874.429843(2.056)	0.07	12.69
TTMbNC	-8904.294538(1.054)	-8904.294785(2.060)	0.32	53.87
TTMbOC	-8924.108913(1.055)	-8924.108996(2.057)	0.11	18.17

Table S9. Calculated HOMA values on the outer benzene rings of BTM- and TTM-based diradicals.[a]

Diradicals	HOMA		J (cm^{-1})	Diradicals	HOMA		J (cm^{-1})
	BS state	T state			BS state	T state	
BTMa	0.612	0.623	926.44	**TTMa**	0.604	0.612	266.81
BTMaN1	0.587	0.597	778.05	**TTMaN1**	0.572	0.577	237.27
BTMaB	0.816	0.846	-440.21	**TTMaB**	0.859	0.865	-85.74
BTMaC	0.923	0.922	23.21	**TTMaC**	0.934	0.934	5.48
BTMaN2	0.818	0.884	-1014.39	**TTMaN2**	0.879	0.900	-304.93
BTMaO	0.910	0.925	-291.69	**TTMaO**	0.930	0.933	-60.24
BTMaBN	0.832	0.843	-251.99	**TTMaBN**	0.846	0.848	-64.62
BTMaNB	0.829	0.842	-337.86	**TTMaNB**	0.851	0.853	-45.57
BTMb	0.565	0.617	-1746.37	**TTMb**	0.609	0.608	-460.37
BTMbN1	0.527	0.593	-1672.11	**TTMbN1**	0.571	0.574	-449.04
BTMbB	0.841	0.828	230.15	**TTMbB**	0.865	0.861	46.18
BTMbC	0.922	0.923	-14.95	**TTMbC**	0.935	0.935	-10.32
BTMbN2	0.864	0.852	331.38	**TTMbN2**	0.893	0.886	113.20
BTMbO	0.922	0.914	166.94	**TTMbO**	0.933	0.931	42.65
BTMbBN	0.842	0.845	4.48	**TTMbBN**	0.837	0.837	9.83

Table S10. Calculated NICS(1)zz values (ppm) on the outer benzene rings of BTM- and TTM-based diradicals in the triplet states.*

Diradicals	NICS(1)zz	J (cm^{-1})	Diradicals	NICS(1)zz	J (cm^{-1})
BTMa	-12.58	926.44	**TTMa**	-16.67	266.81
BTMaN1	-13.31	778.05	**TTMaN1**	-16.47	237.27
BTMaB	-14.49	-420.21	**TTMaB**	-15.01	-85.74
BTMaC	-18.73	23.21	**TTMaC**	-19.14	5.48
BTMaN2	-9.19	-1014.39	**TTMaN2**	-8.04	-304.93
BTMaO	-14.67	-291.69	**TTMaO**	-14.77	-60.24
BTMaBN	-19.61	-251.99	**TTMaBN**	-20.69	-64.62
BTMaNB	-18.92	-337.86	**TTMaNB**	-19.02	-45.57
BTMb	-17.24	-1746.37	**TTMb**	-18.66	-460.37
BTMbN1	-17.82	-1672.11	**TTMbN1**	-18.48	-449.04
BTMbB	-13.66	230.15	**TTMbB**	-14.44	46.18
BTMbC	-18.56	-14.95	**TTMbC**	-20.01	-10.32
BTMbN2	-8.15	331.38	**TTMbN2**	-7.26	113.20
BTMbO	-14.04	166.94	**TTMbO**	-14.36	42.56
BTMbBN	-19.23	4.48	**TTMbBN**	-18.38	9.83

*HOMA and NICS(1)zz values are carried out following the method described in our previous report. (Phys. Chem. Chem. Phys., 2024, 26, 2529–2538)

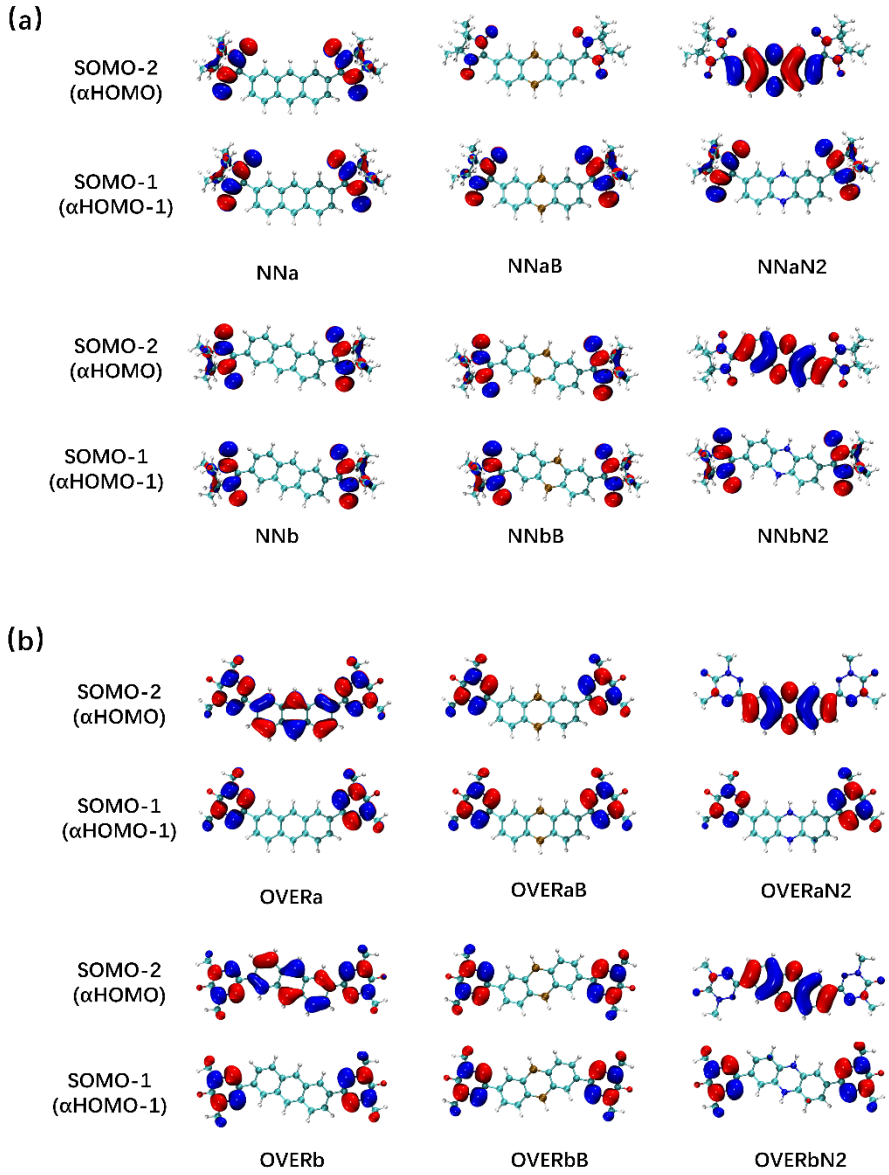

Fig. S4 Electron density distributions of SOMO-1 and SOMO-2 for some analogues of BTMa and BTMb derivatives with NN (a) and OVER (b) as spin sources.