Supporting Information for

Tuning the singlet fission relevant energetic levels of quinoidal bithiophene compounds by means of backbone modifications and functional group introduction

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1. The calculation procedure of multiple diradical character by the PUHF method

The multiple diradical character y_i is evaluated by using the approximate spin-projected spin-unrestricted Hartree-Fock (PUHF) theory， as proposed by Yamaguchi[1]

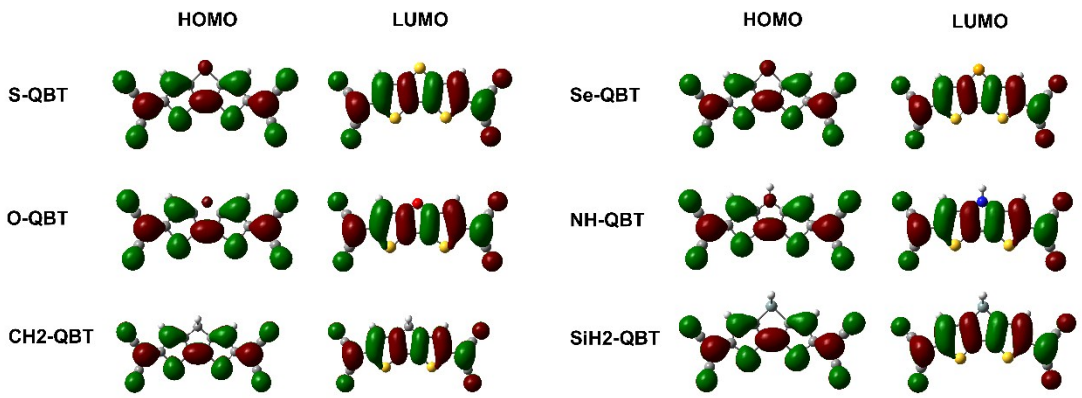
$$y_i = 1 - \frac{2T_i}{1 + T_i^2} \tag{S1}$$

where

$$T_i = \frac{n_{HONO-i} - n_{LUNO+i}}{2} \tag{S2}$$

T_i represents the orbital overlap between the corresponding orbital pairs. n_{HONO-i} and n_{LUNO+i} correspond to the occupation numbers of the *i*-th highest occupied natural orbitals (HOMO-*i*) (i=0,1……) and the *i*-th lowest unoccupied natural orbitals (LUNO+*i*), respectively.

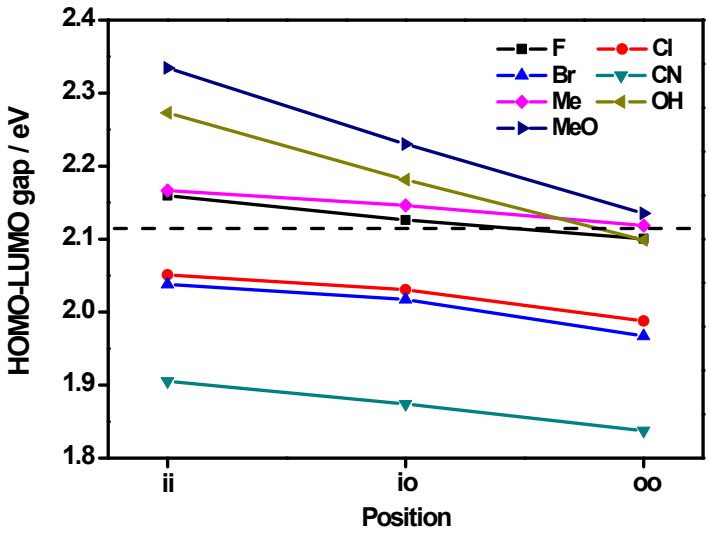
2. **Figure 1S.** HOMO and LUMO electron density distributions of QBT-2 derivatives with heterocyclic attached



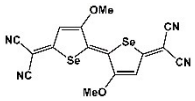
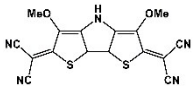
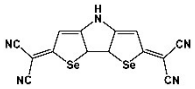
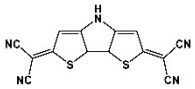
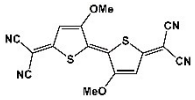
3. Table S1. Dihedral angle of ∠C4-C5-C6-C7 of QBT derivatives with side substituents in S_0/T_1 states.

	ii-R-QBT	io-R-QBT	oo-R-QBT
F	180/180	180/180	180/164
Cl	180/132	180/180	180/165
Br	180/180	180/180	180/167
CN	180/180	180/180	180/167
CF_3	167/126	180/145	180/180
Me	180/129	180/172	180/180
OH	180/180	180/180	180/164
MeO	180/180	180/180	180/164

4. Figure 2S. HOMO-LUMO gaps of QBT-1 derivatives with side substituents. The dashed line indicates the HOMO-LUMO gap of QBT-1 as reference.



5. Table S2**.** Calculated results for ii-MeO-QBS, oo-MeO-QDTP and QDSeP.[a]

Compound		y_0	$E(S_1)$	$E(T_1)$	ΔE_{SF}	HOMO	LUMO	E_{gap}
ii-**MeO**-**QBS**		0	2.351	0.978	0.395	-6.216	-3.877	2.339
oo-**MeO**-**QDTP**		0	2.154	0.693	0.769	-6.249	-4.152	2.097
QDSeP		0	2.002	0.813	0.376	6.442	-4.231	2.211
QDTP[b]		0.287	2.208	0.787	0.634	-6.496	-4.288	2.208
ii-**MeO**-**QBT**[b]		0.247	2.434	0.941	0.552	-6.275	-3.940	2.334

[a]All energies in eV; [b]as reference.

References

(1) K. Yamaguchi, Self-Consistent Field: Theory and Applications; Carbo, R.; Klobukowski, M. eds.; Elsevier: Amsterdam, The Netherands, 1990; p 727