

Supplementary Information for the paper entitled:

**Room Temperature Phosphorescence Based on Triplet-Triplet Energy Transfer in Host-Guest Systems:
Excited-States Alignment and Rational Design from Range-Separated Hybrids**

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This supplementary file includes 13 Tables and 4 Figures.

Table S1. Experimental data (eV) for the H/G systems under study taken from the absorption (acetonitrile, $\epsilon = 35.688$) and phosphorescence (toluene, $\epsilon = 2.3741$) spectra.

H/G	$E_H(T_1)$	$E_G(T_1)$	$E_H(S_1)$	$E_G(S_1)$
BP/AQ	2.94	2.69	4.96	4.92
BP/1,4-AQ	2.94	2.46	4.96	5.35
BP/NAQ	2.94	2.43	4.96	5.20
BP/PAQ	2.94	2.38	4.96	4.12

Table S2. The values of the triplet excitation energies (eV) for the considered host and guest units computed using the proposed OT-RSHs with the BLYP, PBE, and TPSS DFAs and all the combinations of the parameters α and β based on the TD-DFT (TDA) framework.

Molecule	$\alpha = 0.0, \beta = 1.0$			$\alpha = 0.1, \beta = 0.9$		
	BLYP	PBE	TPSS	BLYP	PBE	TPSS
BP	2.35 (2.43)	2.29 (2.37)	2.32 (2.45)	2.35 (2.45)	2.29 (2.40)	2.30 (2.47)
AQ	2.49 (2.52)	2.42 (2.45)	2.48 (2.53)	2.49 (2.54)	2.42 (2.46)	2.48 (2.54)
1,4-AQ	2.19 (2.28)	2.20 (2.29)	2.20 (2.31)	2.16 (2.25)	2.17 (2.27)	1.84 (2.28)
NAQ	2.30 (2.44)	2.34 (2.37)	2.16 (2.46)	2.21 (2.49)	2.16 (2.44)	2.06 (2.49)
PAQ	2.43 (2.46)	2.37 (2.40)	2.44 (2.48)	2.51 (2.59)	2.49 (2.52)	2.50 (2.57)
Molecule	$\alpha = 0.2, \beta = 0.8$			$\alpha = 0.3, \beta = 0.7$		
	BLYP	PBE	TPSS	BLYP	PBE	TPSS
BP	2.34 (2.49)	2.28 (2.44)	2.26 (2.51)	2.29 (2.56)	2.22 (2.50)	2.16 (2.56)
AQ	2.46 (2.59)	2.46 (2.51)	2.31 (2.59)	2.31 (2.70)	2.24 (2.62)	2.13 (2.69)
1,4-AQ	2.15 (2.27)	1.81 (2.29)	1.54 (2.30)	1.52 (2.33)	1.40 (2.35)	1.05 (2.36)
NAQ	2.02 (2.51)	1.94 (2.49)	1.82 (2.48)	1.94 (2.47)	1.86 (2.45)	1.74 (2.44)
PAQ	2.00 (2.60)	1.92 (2.58)	1.79 (2.56)	1.98 (2.56)	1.90 (2.54)	1.78 (2.53)
Molecule	$\alpha = 0.4, \beta = 0.6$					
	BLYP	PBE	TPSS			
BP	2.16 (2.62)	2.08 (2.57)	1.98 (2.62)			
AQ	2.13 (2.79)	2.05 (2.30)	1.93 (2.77)			
1,4-AQ	1.13 (2.29)	0.96 (2.71)	0.27 (2.31)			
NAQ	1.73 (2.45)	1.61 (2.42)	1.47 (2.41)			
PAQ	1.80 (2.53)	1.69 (2.50)	1.56 (2.49)			

Table S3. The values of the triplet excitation energies (eV) for the considered host and guest units within the frameworks of LR-PCM (non-eq), LR-PCM (eq), SS-PCM (non-eq), and SS-PCM (eq) computed using the proposed BLYP-based OT-RSHs based on TDA and all the combinations of the parameters α and β .

Molecule	LR-PCM (non-eq)				
	$\alpha = 0.0, \beta = 1.0$	$\alpha = 0.1, \beta = 0.9$	$\alpha = 0.2, \beta = 0.8$	$\alpha = 0.3, \beta = 0.7$	$\alpha = 0.4, \beta = 0.6$
BP	2.17	2.54	2.59	2.65	2.72
AQ	1.97	2.59	2.64	2.75	2.85
1,4-AQ	1.54	2.15	2.17	2.23	2.18
NAQ	1.85	2.44	2.52	2.46	2.46
PAQ	2.07	2.58	2.62	2.58	2.55

Molecule	LR-PCM (eq)				
	$\alpha = 0.0, \beta = 1.0$	$\alpha = 0.1, \beta = 0.9$	$\alpha = 0.2, \beta = 0.8$	$\alpha = 0.3, \beta = 0.7$	$\alpha = 0.4, \beta = 0.6$
BP	2.17	2.54	2.59	2.65	2.72
AQ	1.97	2.59	2.63	2.75	2.85
1,4-AQ	1.54	2.15	2.17	2.23	2.18
NAQ	1.85	2.44	2.52	2.46	2.46
PAQ	2.07	2.58	2.62	2.58	2.55

Molecule	SS-PCM (non-eq)				
	$\alpha = 0.0, \beta = 1.0$	$\alpha = 0.1, \beta = 0.9$	$\alpha = 0.2, \beta = 0.8$	$\alpha = 0.3, \beta = 0.7$	$\alpha = 0.4, \beta = 0.6$
BP	2.14	2.51	2.55	2.62	2.69
AQ	1.96	2.57	2.63	2.74	2.83
1,4-AQ	1.46	2.04	2.05	2.11	2.07
NAQ	1.75	2.35	2.52	2.40	2.46
PAQ	2.06	2.57	2.62	2.58	2.55

Molecule	SS-PCM (eq)				
	$\alpha = 0.0, \beta = 1.0$	$\alpha = 0.1, \beta = 0.9$	$\alpha = 0.2, \beta = 0.8$	$\alpha = 0.3, \beta = 0.7$	$\alpha = 0.4, \beta = 0.6$
BP	2.14	2.51	2.55	2.62	2.69
AQ	1.96	2.57	2.64	2.74	2.83
1,4-AQ	1.46	2.03	2.05	2.11	2.06
NAQ	1.74	2.34	2.52	2.39	2.45
PAQ	2.06	2.57	2.62	2.58	2.55

Table S4. The values of the triplet excitation energies (eV) for the considered host and guest units within the OT-SRSH framework with the proposed BLYP-based models using TDA and all the combinations of the parameters α and β .

Molecule	OT-SRSH				
	$\alpha = 0.0, \beta = 1.0$	$\alpha = 0.1, \beta = 0.9$	$\alpha = 0.2, \beta = 0.8$	$\alpha = 0.3, \beta = 0.7$	$\alpha = 0.4, \beta = 0.6$
BP	2.23	2.30	2.39	2.49	2.58
AQ	2.18	2.27	2.39	2.55	2.70
1,4-AQ	1.88	1.91	1.97	2.05	2.12
NAQ	2.14	2.19	2.28	2.32	2.39
PAQ	2.24	2.36	2.46	2.47	2.48

Table S5. The values of the singlet excitation energies (eV) for the considered host and guest units computed using the proposed OT-RSHs with the BLYP, PBE, and TPSS DFAs and all the combinations of the parameters α and β based on the TD-DFT (TDA) framework.

Molecule	$\alpha = 0.0, \beta = 1.0$			$\alpha = 0.1, \beta = 0.9$		
	BLYP	PBE	TPSS	BLYP	PBE	TPSS
BP	3.64 (3.66)	3.61 (3.64)	3.70 (3.73)	3.68 (3.70)	3.65 (3.68)	3.74 (3.77)
AQ	3.19 (3.22)	3.15 (3.17)	3.24 (3.26)	3.21 (3.23)	3.16 (3.19)	3.25 (3.26)
1,4-AQ	2.93 (2.96)	2.87 (2.90)	2.98 (3.00)	3.00 (3.02)	2.94 (2.96)	3.04 (3.06)
NAQ	3.08 (3.10)	3.04 (3.06)	3.14 (3.16)	3.17 (3.19)	3.13 (3.15)	3.22 (3.24)
PAQ	3.09 (3.11)	3.05 (3.07)	3.15 (3.17)	3.24 (3.26)	3.20 (3.22)	3.29 (3.31)
Molecule	$\alpha = 0.2, \beta = 0.8$			$\alpha = 0.3, \beta = 0.7$		
	BLYP	PBE	TPSS	BLYP	PBE	TPSS
BP	3.74 (3.77)	3.71 (3.74)	3.80 (3.83)	3.83 (3.86)	3.79 (3.83)	3.88 (3.91)
AQ	3.26 (3.29)	3.22 (3.24)	3.30 (3.33)	3.39 (3.42)	3.34 (3.37)	3.42 (3.45)
1,4-AQ	3.10 (3.13)	3.04 (3.07)	3.14 (3.17)	3.25 (3.28)	3.19 (3.22)	3.27 (3.31)
NAQ	3.38 (3.41)	3.33 (3.36)	3.42 (3.44)	3.41 (3.43)	3.36 (3.39)	3.44 (3.47)
PAQ	3.51 (3.54)	3.47 (3.50)	3.55 (3.57)	3.50 (3.53)	3.46 (3.49)	3.54 (3.57)
Molecule	$\alpha = 0.4, \beta = 0.6$					
	BLYP	PBE	TPSS			
BP	3.93 (3.97)	3.89 (3.94)	3.97 (4.02)			
AQ	3.48 (3.52)	3.43 (3.47)	3.51 (3.54)			
1,4-AQ	3.32 (3.36)	3.26 (3.30)	3.34 (3.38)			
NAQ	3.54 (3.58)	3.50 (3.53)	3.57 (3.61)			
PAQ	3.76 (3.83)	3.79 (3.86)	3.82 (3.89)			

Table S6. Computed values (eV) of the energy difference $E_H(T_1) - E_G(T_1)$ using the BLYP-based OT-RSH with all the combinations of the parameters α and β for the corresponding host and guest units.

H/G System	H \ G	$\alpha = 0.0,$ $\beta = 1.0$	$\alpha = 0.1,$ $\beta = 0.9$	$\alpha = 0.2,$ $\beta = 0.8$	$\alpha = 0.3,$ $\beta = 0.7$	$\alpha = 0.4,$ $\beta = 0.6$
BP/AQ	$\alpha = 0.0, \beta = 1.0$	-0.10	-0.11	-0.16	-0.27	-0.36
BP/1,4-AQ	$\alpha = 0.0, \beta = 1.0$	0.15	0.17	0.15	0.09	0.14
BP/NAQ	$\alpha = 0.0, \beta = 1.0$	-0.01	0.06	-0.09	-0.05	-0.02
BP/PAQ	$\alpha = 0.0, \beta = 1.0$	-0.03	-0.17	-0.18	-0.14	-0.10
BP/AQ	$\alpha = 0.1, \beta = 0.9$	-0.07	-0.08	-0.13	-0.24	-0.34
BP/1,4-AQ	$\alpha = 0.1, \beta = 0.9$	0.17	0.20	0.18	0.12	0.16
BP/NAQ	$\alpha = 0.1, \beta = 0.9$	0.01	-0.04	-0.06	-0.02	0.00
BP/PAQ	$\alpha = 0.1, \beta = 0.9$	-0.01	-0.14	-0.15	-0.11	-0.08
BP/AQ	$\alpha = 0.2, \beta = 0.8$	-0.03	-0.04	-0.09	-0.20	-0.29
BP/1,4-AQ	$\alpha = 0.2, \beta = 0.8$	0.22	0.24	0.22	0.16	0.21
BP/NAQ	$\alpha = 0.2, \beta = 0.8$	0.06	0.01	-0.02	0.02	0.05
BP/PAQ	$\alpha = 0.2, \beta = 0.8$	0.04	-0.10	-0.11	-0.07	-0.03
BP/AQ	$\alpha = 0.3, \beta = 0.7$	0.03	0.02	-0.03	-0.14	-0.23
BP/1,4-AQ	$\alpha = 0.3, \beta = 0.7$	0.28	0.30	0.28	0.22	0.27
BP/NAQ	$\alpha = 0.3, \beta = 0.7$	0.12	0.07	0.04	0.09	0.11
BP/PAQ	$\alpha = 0.3, \beta = 0.7$	0.10	-0.04	-0.05	0.00	0.03
BP/AQ	$\alpha = 0.4, \beta = 0.6$	0.10	0.09	0.04	-0.07	-0.16
BP/1,4-AQ	$\alpha = 0.4, \beta = 0.6$	0.35	0.37	0.35	0.29	0.34
BP/NAQ	$\alpha = 0.4, \beta = 0.6$	0.19	0.14	0.11	0.15	0.18
BP/PAQ	$\alpha = 0.4, \beta = 0.6$	0.17	0.03	0.02	0.06	0.10

Table S7. Computed values (eV) of the energy difference $E_H(T_1) - E_G(T_1)$ using the PBE-based OT-RSH with all the combinations of the parameters α and β for the corresponding host and guest units.

H/G System	H \ G	$\alpha = 0.0,$ $\beta = 1.0$	$\alpha = 0.1,$ $\beta = 0.9$	$\alpha = 0.2,$ $\beta = 0.8$	$\alpha = 0.3,$ $\beta = 0.7$	$\alpha = 0.4,$ $\beta = 0.6$
BP/AQ	$\alpha = 0.0, \beta = 1.0$	-0.08	-0.09	-0.14	-0.25	0.07
BP/1,4-AQ	$\alpha = 0.0, \beta = 1.0$	0.08	0.10	0.09	0.03	-0.33
BP/NAQ	$\alpha = 0.0, \beta = 1.0$	0.00	-0.07	-0.12	-0.08	-0.05
BP/PAQ	$\alpha = 0.0, \beta = 1.0$	-0.02	-0.15	-0.21	-0.17	-0.13
BP/AQ	$\alpha = 0.1, \beta = 0.9$	-0.06	-0.07	-0.11	-0.22	0.10
BP/1,4-AQ	$\alpha = 0.1, \beta = 0.9$	0.10	0.13	0.11	0.05	-0.31
BP/NAQ	$\alpha = 0.1, \beta = 0.9$	0.02	-0.05	-0.10	-0.05	-0.03
BP/PAQ	$\alpha = 0.1, \beta = 0.9$	0.00	-0.13	-0.19	-0.14	-0.11
BP/AQ	$\alpha = 0.2, \beta = 0.8$	-0.01	-0.02	-0.07	-0.18	0.14
BP/1,4-AQ	$\alpha = 0.2, \beta = 0.8$	0.15	0.17	0.15	0.09	-0.27
BP/NAQ	$\alpha = 0.2, \beta = 0.8$	0.07	0.00	-0.05	-0.01	0.02
BP/PAQ	$\alpha = 0.2, \beta = 0.8$	0.04	-0.08	-0.14	-0.10	-0.06
BP/AQ	$\alpha = 0.3, \beta = 0.7$	0.05	0.04	-0.01	-0.12	0.20
BP/1,4-AQ	$\alpha = 0.3, \beta = 0.7$	0.21	0.23	0.22	0.16	-0.20
BP/NAQ	$\alpha = 0.3, \beta = 0.7$	0.13	0.06	0.01	0.05	0.08
BP/PAQ	$\alpha = 0.3, \beta = 0.7$	0.11	-0.02	-0.08	-0.04	0.00
BP/AQ	$\alpha = 0.4, \beta = 0.6$	0.12	0.11	0.06	-0.05	0.27
BP/1,4-AQ	$\alpha = 0.4, \beta = 0.6$	0.28	0.30	0.29	0.23	-0.13
BP/NAQ	$\alpha = 0.4, \beta = 0.6$	0.20	0.13	0.08	0.12	0.15

BP/PAQ	$\alpha = 0.4, \beta = 0.6$	0.18	0.05	-0.01	0.03	0.07
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Table S8. Computed values (eV) of the energy difference $E_H(T_1) - E_G(T_1)$ using the TPSS-based OT-RSH with all the combinations of the parameters α and β for the corresponding host and guest units.

H/G System	H \ G	$\alpha = 0.0,$ $\beta = 1.0$	$\alpha = 0.1,$ $\beta = 0.9$	$\alpha = 0.2,$ $\beta = 0.8$	$\alpha = 0.3,$ $\beta = 0.7$	$\alpha = 0.4,$ $\beta = 0.6$
BP/AQ	$\alpha = 0.0, \beta = 1.0$	-0.09	-0.10	-0.14	-0.24	-0.33
BP/1,4-AQ	$\alpha = 0.0, \beta = 1.0$	0.14	0.16	0.15	0.09	0.13
BP/NAQ	$\alpha = 0.0, \beta = 1.0$	-0.01	-0.04	-0.03	0.01	0.03
BP/PAQ	$\alpha = 0.0, \beta = 1.0$	-0.04	-0.13	-0.12	-0.08	-0.05
BP/AQ	$\alpha = 0.1, \beta = 0.9$	-0.06	-0.07	-0.12	-0.22	-0.30
BP/1,4-AQ	$\alpha = 0.1, \beta = 0.9$	0.16	0.18	0.17	0.11	0.15
BP/NAQ	$\alpha = 0.1, \beta = 0.9$	0.01	-0.02	-0.01	0.03	0.05
BP/PAQ	$\alpha = 0.1, \beta = 0.9$	-0.02	-0.11	-0.10	-0.06	-0.03
BP/AQ	$\alpha = 0.2, \beta = 0.8$	-0.02	-0.04	-0.08	-0.18	-0.27
BP/1,4-AQ	$\alpha = 0.2, \beta = 0.8$	0.20	0.22	0.21	0.15	0.19
BP/NAQ	$\alpha = 0.2, \beta = 0.8$	0.05	0.02	0.03	0.07	0.09
BP/PAQ	$\alpha = 0.2, \beta = 0.8$	0.02	-0.07	-0.06	-0.02	0.01
BP/AQ	$\alpha = 0.3, \beta = 0.7$	0.03	0.02	-0.03	-0.13	-0.21
BP/1,4-AQ	$\alpha = 0.3, \beta = 0.7$	0.25	0.28	0.26	0.20	0.25
BP/NAQ	$\alpha = 0.3, \beta = 0.7$	0.10	0.07	0.08	0.12	0.15
BP/PAQ	$\alpha = 0.3, \beta = 0.7$	0.08	-0.02	-0.01	0.03	0.07
BP/AQ	$\alpha = 0.4, \beta = 0.6$	0.09	0.08	0.03	-0.07	-0.15
BP/1,4-AQ	$\alpha = 0.4, \beta = 0.6$	0.31	0.34	0.32	0.26	0.30

BP/NAQ	$\alpha = 0.4, \beta = 0.6$	0.16	0.13	0.14	0.18	0.20
BP/PAQ	$\alpha = 0.4, \beta = 0.6$	0.13	0.04	0.05	0.09	0.12

Table S9. The excitation energies, values of indexes as well as the character of the triplet excited-states of the host and guest units computed using the BLYP-based OT-RSHs. M_{AC} values are reported for the CT states. For the AQ and PAQ systems, visualizations of the electron and hole distributions have also been taken into account.

Molecule	$\alpha = 0.0, \beta = 1.0$					$\alpha = 0.1, \beta = 0.9$				
	E (eV)	D (Å)	M_{AC} (eV)	Δr (Å)	Character	E (eV)	D (Å)	M_{AC} (eV)	Δr (Å)	Character
BP	2.43	0.93	-	1.70	L	2.45	0.92	-	1.47	L
AQ	2.52	0.00	-	0.00	L	2.54	0.00	-	0.00	L
1,4-AQ	2.28	2.35	0.447	5.26	CT	2.25	1.96	-0.740	5.64	CT
NAQ	2.44	0.10	-	0.58	L	2.49	1.85	-1.060	6.11	CT
PAQ	2.46	0.00	-	0.00	L	2.59	0.00	-	0.00	L
Molecule	$\alpha = 0.2, \beta = 0.8$					$\alpha = 0.3, \beta = 0.7$				
	E (eV)	D (Å)	M_{AC} (eV)	Δr (Å)	Character	E (eV)	D (Å)	M_{AC} (eV)	Δr (Å)	Character
BP	2.49	0.90	-	1.05	L	2.56	0.85	-	0.88	L
AQ	2.59	0.00	-	0.00	L	2.70	0.00	-	0.00	L
1,4-AQ	2.27	1.94	-0.769	5.61	CT	2.33	1.86	-0.846	5.56	CT
NAQ	2.51	0.20	-63.163	3.19	CT	2.47	0.28	-43.871	3.27	CT
PAQ	2.60	0.00	-	0.00	L	2.56	0.00	-	0.00	L
Molecule	$\alpha = 0.4, \beta = 0.6$									
	E (eV)	D (Å)	M_{AC} (eV)	Δr (Å)	Character					
BP	2.62	0.76	-	0.77	L					
AQ	2.79	0.00	-	0.00	L					

1,4-AQ	2.29	1.90	-0.908	5.55	CT
NAQ	2.45	0.18	-71.228	3.14	CT
PAQ	2.53	0.00	-	0.00	L

Table S10. The computed values (eV) of the TTET gaps using the best OT-RSH with different basis sets for the H/G systems under study. Also given as the boldface in the last rows are the corresponding statistical metrics.

H/G System	6-31+G(d)	6-311++G(d,p)	6-311++G(2df,2p)	TZVP
BP/AQ	0.10	0.09	0.11	0.08
BP/1,4-AQ	0.35	0.33	0.34	0.30
BP/NAQ	0.19	0.18	0.20	0.16
BP/PAQ	0.17	0.16	0.19	0.14
MSD	-0.25	-0.26	-0.24	-0.28
MAD	0.25	0.26	0.24	0.28

Table S11. The computed values (eV) of the TTET gaps using the best proposed OT-RSH with different integration grids for the H/G systems under study. Also given as the boldface in the last rows are the corresponding statistical metrics.

H/G System	<i>FineGrid</i>	<i>UltraFineGrid</i>	<i>SuperFineGrid</i>
BP/AQ	0.10	0.10	0.10
BP/1,4-AQ	0.35	0.35	0.35
BP/NAQ	0.19	0.19	0.19
BP/PAQ	0.17	0.17	0.17
MSD	-0.25	-0.25	-0.25
MAD	0.25	0.25	0.25

Table S12. The computed values (eV) of the TTET gap for the H/G systems under study using the BLYP-based OT-RSH ($\alpha = 0.4, \beta = 0.6/\alpha = 0.0, \beta = 1.0$) within the frameworks of LR-PCM (eq), LR-PCM (non-eq), SS-PCM (eq), and SS-PCM (non-eq).

H/G System	LR-PCM (non-eq)	LR-PCM (eq)	SS-PCM (non-eq)	SS-PCM (eq)
BP/AQ	0.75	0.75	0.73	0.73
BP/1,4-AQ	1.17	1.17	1.22	1.23
BP/NAQ	0.86	0.86	0.94	0.95
BP/PAQ	0.65	0.65	0.63	0.63

Table S13. Optimally tuned values of the range-separation parameter for the theoretically designed hosts (**I-IV**) and guests (**V-XII**). All values are in Bohr⁻¹.

Molecule	μ (Bohr ⁻¹)
I	0.1308
II	0.1222
III	0.1334
IV	0.1296
V	0.2178
VI	0.1953
VII	0.1849
VIII	0.1744
IX	0.2556
X	0.2481
XI	0.2079
XII	0.2029

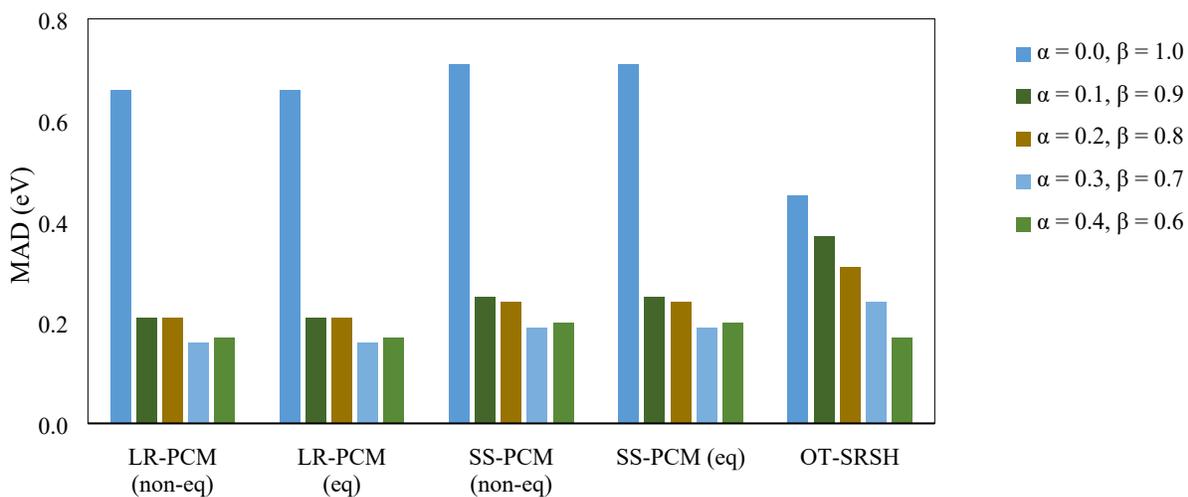


Figure S1. MADs on the performance of the proposed BLYP-based OT-RSHs based on TDA and all the combinations of the parameters α and β for predicting the triplet excitation energies for the considered host and guest units within the frameworks of LR-PCM (non-eq), LR-PCM (eq), SS-PCM (non-eq), SS-PCM (eq), and OT-SRSH.

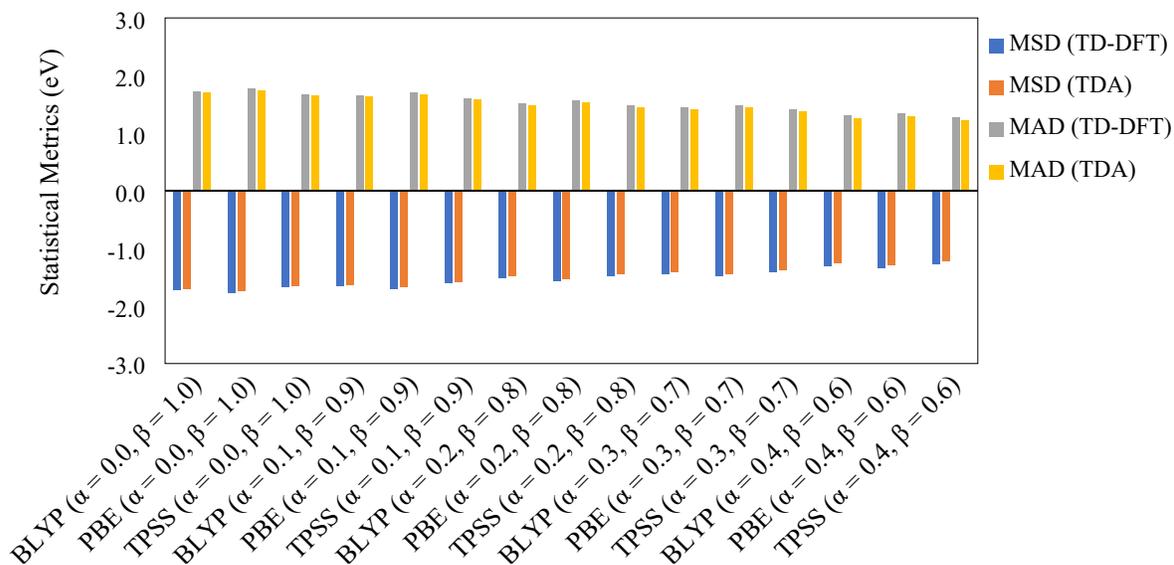


Figure S2. Statistical metrics (eV) on the performance of the proposed OT-RSHs with the BLYP, PBE, and TPSS DFAs and all the combinations of the parameters α and β based on the TD-DFT and TDA for the calculations of the singlet excitation energies of the considered host and guest units.

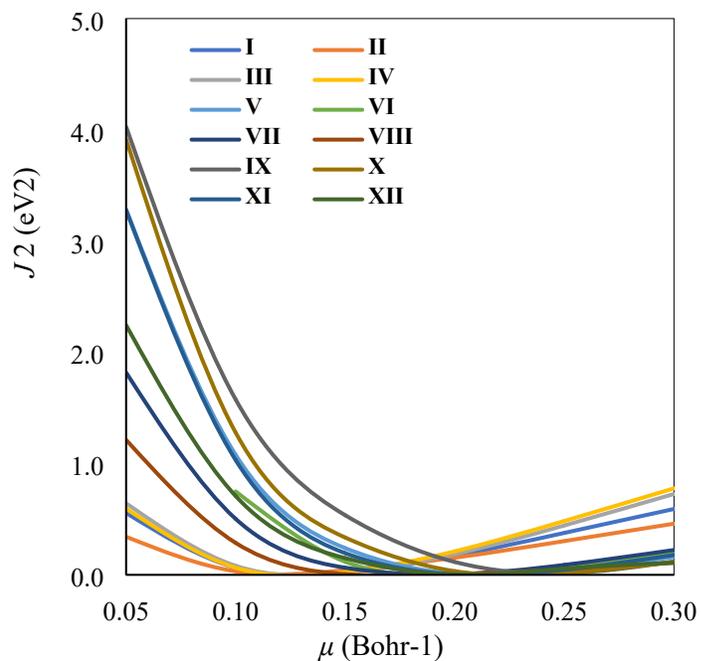


Figure S3. Plot of the target function J^2 versus the range-separation parameter μ for the theoretically designed hosts (I-IV) and guests (V-XII).

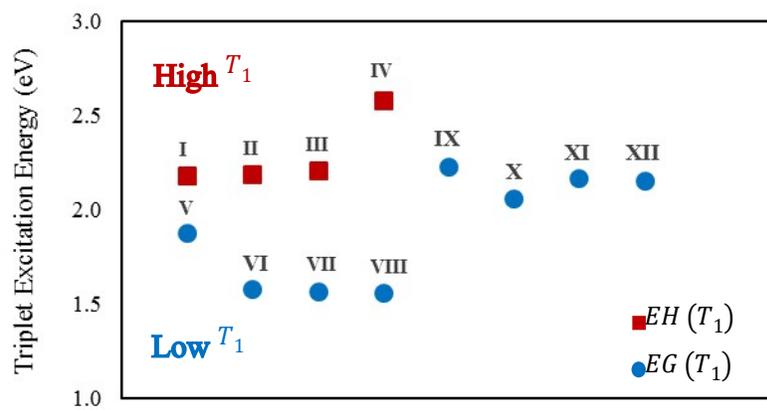


Figure S4. Graphical representation of the triplet excitation energies computed using the best proposed OT-RSH for the theoretically designed host and guest units.