Supporting Information for the paper entitled:

Toward photophysical characteristics of triplet-triplet annihilation photon upconversion: A promising protocol from the perspective of optimally tuned range-separated hybrids

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Table S1. The experimentally known sensitizer/annihilator pairs under study along with their measured values of quantum yields (QY) for the intersystem crossing (ISC) of the sensitizers, fluorescence of the annihilators, and triplet–triplet annihilation photon upconversion (TTA-UC), as well as the triplet-triplet energy transfer (TTET) gaps in the corresponding solvents.[1-6]

	Biacetyl/PPO	ZnOEP/DPA	PdOEP/DPA	PtOEP/DPA
ISC QY for the sensitizer	0.855	0.959	1.000	1.000
Fluorescence QY for the annihilator	0.850	0.960	0.960	0.960
TTA-UC QY for the pair	0.0058	0.060	0.125	0.150
TTET gap	-0.1	0.01	0.08	0.14
Solvent	Benzene	Chlorobenzene	Chlorobenzene	Chlorobenzene

Table S2. The computed TD-DFT (TDA) values of the triplet excitation energies using the TPSS-based OT-RSHs for the sensitizers and annihilators under study. The reference values are also given. All values are in eV.

	Ref.	$\alpha = 0.00,\ \beta = 1.00$	$\alpha = 0.10,\ \beta = 0.90$	$\alpha = 0.20,\ \beta = 0.80$	$\alpha = 0.30,\ \beta = 0.70$
Sensitizers					
Biacetyl	2.38	2.24 (2.31)	2.29 (2.38)	2.35 (2.44)	2.40 (2.51)
ZnOEP	1.78	1.60 (1.88)	1.47 (1.86)	1.30 (1.84)	1.05 (1.82)
PdOEP	1.85	1.66 (2.00)	1.52 (1.97)	1.33 (1.94)	1.08 (1.91)
PtOEP	1.91	1.77 (2.07)	1.64 (2.05)	1.47 (2.02)	1.25 (1.99)
$[Ru(bpy)_3]^{2+}$	1.97	2.33 (2.36)	2.57 (2.64)	2.69 (2.87)	2.66 (3.06)
$Ir(ppy)_3$	2.38	2.58 (2.63)	2.69 (2.79)	2.71 (2.91)	2.65 (3.00)
Annihilators					
PPO	2.48	2.75 (3.02)	2.65 (3.02)	2.52 (3.01)	2.36 (2.99)
DPA	1.77	1.81 (2.15)	1.68 (2.14)	1.51 (2.13)	1.26 (2.12)
Perylene	1.55	1.58 (2.01)	1.43 (2.01)	1.23 (2.00)	0.93 (1.99)
Pyrene	2.09	2.16 (2.59)	2.01 (2.59)	1.82 (2.57)	1.58 (2.56)
1-CBPEA	1.36	1.31 (1.60)	1.20 (1.61)	1.03 (1.62)	0.76 (1.62)
BA	2.04	2.14 (2.52)	2.00 (2.51)	1.82 (2.50)	1.59 (2.48)

	Ref.	$\alpha = 0.40,\ \beta = 0.60$	$\alpha = 0.50,\ \beta = 0.50$	$\alpha = 0.60,\ \beta = 0.40$
Sensitizers				
Biacetyl	2.38	2.45 (2.58)	2.50 (2.65)	2.55 (2.72)
ZnOEP	1.78	0.66 (1.79)	-0.57 (1.75)	-1.09 (1.71)
PdOEP	1.85	0.70 (1.88)	-0.53 (1.84)	-1.06 (1.79)
PtOEP	1.91	0.93 (1.96)	0.30 (1.92)	-.087 (1.87)
$[Ru(bpy)_3]^{2+}$	1.97	2.52 (3.15)	2.29 (3.10)	1.98 (3.01)
$Ir(ppy)_3$	2.38	2.51 (3.07)	2.31 (3.10)	2.05 (3.12)
Annihilators				
PPO	2.48	2.16 (2.97)	1.91 (2.92)	1.58 (2.93)
DPA	1.77	0.90 (2.11)	-0.31 (2.10)	-1.06 (2.08)
Perylene	1.55	0.36 (1.98)	-0.84 (1.96)	-1.29 (1.95)
Pyrene	2.09	1.24 (2.54)	0.69 (2.95)	-0.82 (2.50)
1-CBPEA	1.36	-0.16 (1.62)	-0.87 (1.62)	-1.27 (1.62)
BA	2.04	1.27 (2.46)	0.76 (2.44)	-0.74 (2.42)

Table S3. The values of MSDs (eV) of the proposed TPSS-based OT-RSHs in the prediction of the triplet-triplet energy transfer gaps of the experimental sensitizer/annihilator pairs under study. Different combinations of α and β parameters for the annihilators and sensitizers are given in the row and column, respectively.

	$\alpha = 0.00$, $\beta = 1.00$	$\alpha = 0.10$, $\beta = 0.90$	$\alpha = 0.20$, $\beta = 0.80$	$\alpha = 0.30$, $\beta = 0.70$	$\alpha = 0.40$, $\beta = 0.60$	$\alpha = 0.50$, $\beta = 0.50$	$\alpha = 0.60$, $\beta = 0.40$
$\alpha = 0.00$, $\beta = 1.00$	-0.01	0.11	0.33	0.50	0.82	1.79	2.43
$\alpha = 0.10$, $\beta = 0.90$	- 0.01	0.11	0.27	0.50	0.82	1.79	2.43
$\alpha = 0.20$, $\beta = 0.80$	- 0.02	0.11	0.27	0.49	0.81	1.79	2.43
$\alpha = 0.30$, $\beta = 0.70$	- 0.02	0.10	0.27	0.49	0.81	1.78	2.43
$\alpha = 0.40$, $\beta = 0.60$	- 0.03	0.09	0.26	0.48	0.80	1.78	2.42
$\alpha = 0.50$, $\beta = 0.50$	- 0.04	0.08	0.26	0.47	0.79	1.76	2.41
$\alpha = 0.60$, $\beta = 0.40$	- 0.06	0.07	0.23	0.45	0.78	1.75	2.39

Table S4. The values of MADs (eV) of the proposed TPSS-based OT-RSHs in the prediction of the triplet-triplet energy transfer gaps of the experimental sensitizer/annihilator pairs under study. Different combinations of α and β parameters for the annihilators and sensitizers are given in the row and column, respectively.

	$\alpha = 0.00$, $\beta = 1.00$	$\alpha = 0.10$, $\beta = 0.90$	$\alpha = 0.20$, $\beta = 0.80$	$\alpha = 0.30$, $\beta = 0.70$	$\alpha = 0.40$, $\beta = 0.60$	$\alpha = 0.50$, $\beta = 0.50$	$\alpha = 0.60$, $\beta = 0.40$
$\alpha = 0.00$, $\beta = 1.00$	0.15	0.23	0.33	0.50	0.82	1.79	2.43
$\alpha = 0.10$, $\beta = 0.90$	0.12	0.20	0.30	0.50	0.82	1.79	2.43
$\alpha = 0.20$, $\beta = 0.80$	0.09	0.16	0.27	0.49	0.81	1.79	2.43
$\alpha = 0.30$, $\beta = 0.70$	0.05	0.12	0.27	0.49	0.81	1.78	2.43
$\alpha = 0.40$, $\beta = 0.60$	0.03	0.09	0.26	0.48	0.80	1.78	2.42
$\alpha = 0.50$, $\beta = 0.50$	0.04	0.08	0.26	0.47	0.79	1.76	2.41
$\alpha = 0.60$, $\beta = 0.40$	0.09	0.07	0.23	0.45	0.78	1.75	2.39

Table S5. The values of MaxADs (eV) of the proposed TPSS-based OT-RSHs in the prediction of the triplet-triplet energy transfer gaps of the experimental sensitizer/annihilator pairs under study. Different combinations of α and β parameters for the annihilators and sensitizers are given in the row and column, respectively.

	$\alpha = 0.00$, $\beta = 1.00$	$\alpha = 0.10$, $\beta = 0.90$	$\alpha = 0.20$, $\beta = 0.80$	$\alpha = 0.30$, $\beta = 0.70$	$\alpha = 0.40$, $\beta = 0.60$	$\alpha = 0.50$, $\beta = 0.50$	$\alpha = 0.60$, $\beta = 0.40$
$\alpha = 0.00$, $\beta = 1.00$	0.34	0.25	0.43	0.67	1.03	2.25	2.99
$\alpha = 0.10$, $\beta = 0.90$	0.27	0.23	0.40	0.65	1.01	2.22	2.97
$\alpha = 0.20$, $\beta = 0.80$	0.20	0.20	0.38	0.62	0.99	2.20	2.94
$\alpha = 0.30$, $\beta = 0.70$	0.13	0.17	0.35	0.59	0.95	2.17	2.91
$\alpha = 0.40$, $\beta = 0.60$	0.07	0.13	0.31	0.55	0.92	2.13	2.88
$\alpha = 0.50$, $\beta = 0.50$	0.07	0.10	0.56	0.52	0.88	2.09	2.84
$\alpha = 0.60$, $\beta = 0.40$	0.11	0.17	0.30	0.47	0.84	2.05	2.79

Table S6. The values of MinADs (eV) of the proposed TPSS-based OT-RSHs in the prediction of the triplet-triplet energy transfer gaps of the experimental sensitizer/annihilator pairs under study. Different combinations of α and β parameters for the annihilators and sensitizers are given in the row and column, respectively.

	$\alpha = 0.00$, $\beta = 1.00$	$\alpha = 0.10$, $\beta = 0.90$	$\alpha = 0.20$, $\beta = 0.80$	$\alpha = 0.30$, $\beta = 0.70$	$\alpha = 0.40$, $\beta = 0.60$	$\alpha = 0.50$, $\beta = 0.50$	$\alpha = 0.60$, $\beta = 0.40$
$\alpha = 0.00$, $\beta = 1.00$	0.06	0.19	0.11	0.05	0.25	0.50	0.83
$\alpha = 0.10$, $\beta = 0.90$	0.04	0.17	0.04	0.12	0.32	0.57	0.90
$\alpha = 0.20$, $\beta = 0.80$	0.02	0.10	0.02	0.18	0.38	0.64	0.97
$\alpha = 0.30$, $\beta = 0.70$	0.01	0.04	0.09	0.25	0.45	0.71	1.04
$\alpha = 0.40$, $\beta = 0.60$	0.00	0.03	0.16	0.32	0.52	0.77	1.10
$\alpha = 0.50$, $\beta = 0.50$	0.00	0.06	0.15	0.39	0.59	0.84	1.17
$\alpha = 0.60$, $\beta = 0.40$	0.07	0.02	0.19	0.44	0.66	0.91	1.24

Table S7. The values of RMSDs (eV) of the proposed TPSS-based OT-RSHs in the prediction of the triplet-triplet energy transfer gaps of the experimental sensitizer/annihilator pairs under study. Different combinations of α and β parameters for the annihilators and sensitizers are given in the row and column, respectively.

	$\alpha = 0.00$, $\beta = 1.00$	$\alpha = 0.10$, $\beta = 0.90$	$\alpha = 0.20$, $\beta = 0.80$	$\alpha = 0.30$, $\beta = 0.70$	$\alpha = 0.40$, $\beta = 0.60$	$\alpha = 0.50$, $\beta = 0.50$	$\alpha = 0.60$, $\beta = 0.40$
$\alpha = 0.00$, $\beta = 1.00$	0.19	0.23	0.35	0.56	0.88	1.94	2.60
$\alpha = 0.10$, $\beta = 0.90$	0.15	0.20	0.33	0.54	0.87	1.93	2.59
$\alpha = 0.20$, $\beta = 0.80$	0.11	0.16	0.31	0.53	0.84	1.91	2.57
$\alpha = 0.30$, $\beta = 0.70$	0.07	0.13	0.29	0.51	0.84	1.89	2.55
$\alpha = 0.40$, $\beta = 0.60$	0.04	0.10	0.22	0.49	0.82	1.87	2.53
$\alpha = 0.50$, $\beta = 0.50$	0.05	0.08	0.31	0.47	0.80	1.84	2.51
$\alpha = 0.60$, $\beta = 0.40$	0.09	0.09	0.24	0.45	0.78	1.82	2.48

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