Supporting Information for the paper entitled:

Toward Highly Efficient Hyperfluorescence-based Emitters through Excited-States Alignment Using Novel Optimally Tuned Range-Separated Models

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Table S1. The computed values of the singlet excitation energies within the frameworks of the OT-RSHs, OT-RSHs-PCM, and OT-SRSHs based on the BLYP DFA alongside the corresponding experimental data (eV) for the experimentally known FEs under study. Also given in the table are the related statistical metrics in boldface.

Functionals	Emitter	S_1^{FE}	S_1^{FE} (exp.)	**MSD**	**MAD**	**RMSD**
OT-RSH $\alpha = 0.0, \beta = 1.0$	TBPe	2.97	2.69[a]	**0.13**	**0.20**	**0.22**
	TTPA	2.19	2.34[a]			
	Terrylene	2.44	2.16[b]			
	TBRb	2.28	2.18[a]			
OT-RSH $\alpha = 0.1, \beta = 0.9$	TBPe	3.00	2.69[a]	**0.17**	**0.19**	**0.22**
	TTPA	2.30	2.34[a]			
	Terrylene	2.45	2.16[b]			
	TBRb	2.30	2.18[a]			
OT-RSH $\alpha = 0.2, \beta = 0.8$	TBPe	3.04	2.69[a]	**0.22**	**0.22**	**0.25**
	TTPA	2.43	2.34[a]			
	Terrylene	2.48	2.16[b]			
	TBRb	2.32	2.18[a]			
OT-RSH $\alpha = 0.3, \beta = 0.7$	TBPe	3.08	2.69[a]	**0.28**	**0.28**	**0.29**
	TTPA	2.56	2.34[a]			
	Terrylene	2.50	2.16[b]			
	TBRb	2.34	2.18[a]			
OT-RSH $\alpha = 0.4, \beta = 0.6$	TBPe	3.12	2.69[a]	**0.34**	**0.34**	**0.35**
	TTPA	2.71	2.34[a]			
	Terrylene	2.52	2.16[b]			
	TBRb	2.36	2.18[a]			
OT-RSH-PCM $\alpha = 0.0, \beta = 1.0$	TBPe	2.87	2.69[a]	**0.04**	**0.11**	**0.13**
	TTPA	2.19	2.34[a]			
	Terrylene	2.25	2.16[b]			
	TBRb	2.22	2.18[a]			
OT-RSH-PCM $\alpha = 0.1, \beta = 0.9$	TBPe	2.90	2.69[a]	**0.08**	**0.10**	**0.12**
	TTPA	2.30	2.34[a]			
	Terrylene	2.26	2.16[b]			
	TBRb	2.24	2.18[a]			
OT-RSH-PCM $\alpha = 0.2, \beta = 0.8$	TBPe	2.93	2.69[a]	**0.13**	**0.13**	**0.15**
	TTPA	2.42	2.34[a]			
	Terrylene	2.28	2.16[b]			
	TBRb	2.26	2.18[a]			
	TBPe	2.97	2.69[a]			

OT-RSH-PCM	TTPA	2.55	2.34[a]	**0.18**	**0.18**	**0.19**
$\alpha = 0.3, \beta = 0.7$	Terrylene	2.30	2.16[b]			
	TBRb	2.27	2.18[a]			
	TBPe	3.01	2.69[a]			
OT-RSH-PCM	TTPA	2.69	2.34[a]	**0.24**	**0.24**	**0.26**
$\alpha = 0.4, \beta = 0.6$	Terrylene	2.32	2.16[b]			
	TBRb	2.30	2.18[a]			
	TBPe	2.81	2.69[a]			
OT-SRSH	TTPA	1.79	2.34[a]	**-0.09**	**0.23**	**0.29**
$\alpha = 0.0, \beta = 0.42$	Terrylene	2.32	2.16[b]			
	TBRb	2.10	2.18[a]			
	TBPe	2.87	2.69[a]			
OT-SRSH	TTPA	1.96	2.34[a]	**-0.01**	**0.20**	**0.23**
$\alpha = 0.1, \beta = 0.32$	Terrylene	2.35	2.16[b]			
	TBRb	2.15	2.18[a]			
	TBPe	2.94	2.69[a]			
OT-SRSH	TTPA	2.15	2.34[a]	**0.08**	**0.18**	**0.20**
$\alpha = 0.2, \beta = 0.22$	Terrylene	2.40	2.16[b]			
	TBRb	2.21	2.18[a]			
	TBPe	3.00	2.69[a]			
OT-SRSH	TTPA	2.36	2.34[a]	**0.17**	**0.17**	**0.21**
$\alpha = 0.3, \beta = 0.12$	Terrylene	2.44	2.16[b]			
	TBRb	2.27	2.18[a]			
	TBPe	3.07	2.69[a]			
OT-SRSH	TTPA	2.59	2.34[a]	**0.28**	**0.28**	**0.29**
$\alpha = 0.4, \beta = 0.02$	Terrylene	2.49	2.16[b]			
	TBRb	2.34	2.18[a]			

[a] H. Nakanotani, T. Higuchi, T. Furukawa, K. Masui, K. Morimoto, M. Numata, H. Tanaka, Y. Sagara, T. Yasuda and C. Adachi, High-Efficiency Organic Light-Emitting Diodes with Fluorescent Emitters, *Nat. Commun.*, 2014, **5**, 4016-4023.

[b] Y. Avlasevich, C. Kohl and K. Müllen, Facile Synthesis of Terrylene and Its Isomer Benzoindenoperylene, *J. Mater. Chem.*, 2006, **16**, 1053-1057.

Table S2. The computed values of the excitation energies (eV) using the BLYP-based OT-RSHs for the experimentally known FEs under study.

OT-RSHs	Emitter	S_1^{FE}	T_1^{FE}	T_2^{FE}	T_3^{FE}
BLYP $\alpha = 0.0, \beta = 1.0$	TBPe	2.97	1.47	2.93	3.17
	TTPA	2.19	1.38	2.19	2.28
	Terrylene	2.44	0.96	2.29	2.53
	TBRb	2.28	0.91	2.31	2.94
BLYP $\alpha = 0.1, \beta = 0.9$	TBPe	3.00	1.45	2.93	3.17
	TTPA	2.30	1.37	2.30	2.39
	Terrylene	2.45	0.94	2.28	2.53
	TBRb	2.30	0.88	2.31	2.98
BLYP $\alpha = 0.2, \beta = 0.8$	TBPe	3.04	1.44	2.93	3.18
	TTPA	2.43	1.37	2.43	2.51
	Terrylene	2.48	0.92	2.28	2.53
	TBRb	2.32	0.84	2.30	3.02
BLYP $\alpha = 0.3, \beta = 0.7$	TBPe	3.08	1.42	2.92	3.18
	TTPA	2.56	1.36	2.57	2.65
	Terrylene	2.50	0.90	2.27	2.53
	TBRb	2.34	0.80	2.29	3.06
BLYP $\alpha = 0.4, \beta = 0.6$	TBPe	3.12	1.40	2.92	3.18
	TTPA	2.71	1.34	2.73	2.80
	Terrylene	2.52	0.88	2.26	2.53
	TBRb	2.36	0.76	2.28	3.10

Table S3. The computed values of the excitation energies (eV) using the BLYP-based OT-RSHs-PCM for the experimentally known FEs under study.

OT-RSHs-PCM	Emitter	S_1^{FE}	T_1^{FE}	T_2^{FE}	T_3^{FE}
BLYP $\alpha = 0.0, \beta = 1.0$	TBPe	2.87	1.47	2.94	3.17
	TTPA	2.19	1.37	2.22	2.30
	Terrylene	2.25	0.96	2.29	2.53
	TBRb	2.22	0.91	2.32	2.94
BLYP $\alpha = 0.1, \beta = 0.9$	TBPe	2.90	1.46	2.93	3.18
	TTPA	2.30	1.37	2.34	2.41
	Terrylene	2.26	0.94	2.28	2.53
	TBRb	2.24	0.88	2.31	2.98
BLYP $\alpha = 0.2, \beta = 0.8$	TBPe	2.93	1.44	2.93	3.18
	TTPA	2.42	1.36	2.46	2.53
	Terrylene	2.28	0.93	2.28	2.53
	TBRb	2.26	0.84	2.30	3.02
BLYP $\alpha = 0.3, \beta = 0.7$	TBPe	2.97	1.43	2.93	3.19
	TTPA	2.55	1.35	2.60	2.66
	Terrylene	2.30	0.91	2.27	2.53
	TBRb	2.27	0.80	2.29	3.06
BLYP $\alpha = 0.4, \beta = 0.6$	TBPe	3.01	1.41	2.93	3.19
	TTPA	2.69	1.34	2.76	2.82
	Terrylene	2.32	0.89	2.27	2.53
	TBRb	2.30	0.76	2.28	3.11

Table S4. The computed values of the excitation energies (eV) using the BLYP-based OT-SRSHs for the experimentally known FEs under study.

OT-SRSHs	Emitter	S_1^{FE}	T_1^{FE}	T_2^{FE}	T_3^{FE}
	TBPe	2.81	1.40	2.85	3.08
BLYP	TTPA	1.79	1.30	1.77	1.94
$\alpha = 0, \beta = 0.42$	Terrylene	2.32	0.89	2.21	2.42
	TBRb	2.10	0.88	2.26	2.77
	TBPe	2.87	1.40	2.86	3.09
BLYP	TTPA	1.96	1.32	1.93	2.06
$\alpha = 0.1, \beta = 0.32$	Terrylene	2.35	0.88	2.22	2.44
	TBRb	2.15	0.85	2.27	2.85
	TBPe	2.94	1.39	2.87	3.11
BLYP	TTPA	2.15	1.33	2.12	2.22
$\alpha = 0.2, \beta = 0.22$	Terrylene	2.40	0.88	2.23	2.46
	TBRb	2.21	0.82	2.27	2.93
	TBPe	3.00	1.38	2.88	3.13
BLYP	TTPA	2.36	1.33	2.34	2.43
$\alpha = 0.3, \beta = 0.12$	Terrylene	2.44	0.87	2.24	2.47
	TBRb	2.27	0.79	2.27	3.00
	TBPe	3.07	1.38	2.89	3.15
BLYP	TTPA	2.59	1.33	2.60	2.67
$\alpha = 0.4, \beta = 0.02$	Terrylene	2.49	0.86	2.24	2.49
	TBRb	2.34	0.75	2.26	3.07

Table S5. The computed values of the excitation energies (eV) using the PBE-based OT-RSHs-PCM for the experimentally known FEs under study.

OT-RSHs-PCM	Emitter	S_1^{FE}	T_1^{FE}	T_2^{FE}	T_3^{FE}
PBE $\alpha = 0, \beta = 1.0$	TBPe	2.89	1.47	2.93	3.17
	TTPA	2.17	1.35	2.19	2.28
	Terrylene	2.26	0.96	2.28	2.52
	TBRb	2.22	0.90	2.30	2.94
PBE $\alpha = 0.1, \beta = 0.9$	TBPe	2.92	1.45	2.93	3.17
	TTPA	2.28	1.35	2.31	2.38
	Terrylene	2.27	0.94	2.28	2.52
	TBRb	2.24	0.86	2.30	2.98
PBE $\alpha = 0.2, \beta = 0.8$	TBPe	2.95	1.44	2.92	3.17
	TTPA	2.39	1.35	2.43	2.49
	Terrylene	2.30	0.92	2.27	2.52
	TBRb	2.26	0.82	2.29	3.02
PBE $\alpha = 0.3, \beta = 0.7$	TBPe	2.99	1.42	2.92	3.18
	TTPA	2.52	1.34	2.57	2.63
	Terrylene	2.31	0.90	2.26	2.52
	TBRb	2.28	0.78	2.28	3.06
PBE $\alpha = 0.4, \beta = 0.6$	TBPe	3.02	1.40	2.91	3.18
	TTPA	2.67	1.32	2.73	2.78
	Terrylene	2.34	0.88	2.25	2.52
	TBRb	2.31	0.74	2.26	3.11

Table S6. The computed values of the excitation energies (eV) using the TPSS-based OT-RSHs-PCM for the experimentally known FEs under study.

OT-RSHs-PCM	Emitter	S_1^{FE}	T_1^{FE}	T_2^{FE}	T_3^{FE}
	TBPe	2.91	1.45	2.93	3.17
TPSS	TTPA	2.24	1.35	2.27	2.34
$\alpha = 0, \beta = 1.0$	Terrylene	2.28	0.94	2.28	2.52
	TBRb	2.24	0.87	2.29	2.97
	TBPe	2.93	1.44	2.93	3.17
TPSS	TTPA	2.34	1.34	2.37	2.44
$\alpha = 0.1, \beta = 0.9$	Terrylene	2.29	0.92	2.27	2.52
	TBRb	2.26	0.83	2.29	3.01
	TBPe	2.97	1.42	2.92	3.18
TPSS	TTPA	2.46	1.34	2.49	2.55
$\alpha = 0.2, \beta = 0.8$	Terrylene	2.31	0.91	2.27	2.52
	TBRb	2.27	0.80	2.28	3.05
	TBPe	3.00	1.41	2.92	3.18
TPSS	TTPA	2.58	1.33	2.63	2.68
$\alpha = 0.3, \beta = 0.7$	Terrylene	2.32	0.89	2.26	2.52
	TBRb	2.29	0.76	2.27	3.09
	TBPe	3.04	1.39	2.91	3.18
TPSS	TTPA	2.72	1.31	2.78	2.83
$\alpha = 0.4, \beta = 0.6$	Terrylene	2.35	0.87	2.25	2.52
	TBRb	2.31	0.72	2.25	3.13

Table S7. The computed values of the singlet-triplet energy gaps (eV) using the PBE-based OT-RSHs-PCM for the experimentally known FEs under study.

OT-RSHs-PCM	Emitter	$\Delta E_{S_1T_1}$	$\Delta E_{S_1T_2}$	$\Delta E_{S_1T_3}$
PBE $\alpha = 0, \beta = 1.0$	TBPe	1.42	-0.04	-0.28
	TTPA	0.81	-0.03	-0.11
	Terrylene	1.31	-0.02	-0.26
	TBRb	1.33	-0.08	-0.72
PBE $\alpha = 0.1, \beta = 0.9$	TBPe	1.46	-0.01	-0.26
	TTPA	0.92	-0.03	-0.10
	Terrylene	1.34	0.00	-0.25
	TBRb	1.38	-0.05	-0.74
PBE $\alpha = 0.2, \beta = 0.8$	TBPe	1.51	0.03	-0.22
	TTPA	1.05	-0.04	-0.10
	Terrylene	1.38	0.03	-0.23
	TBRb	1.44	-0.03	-0.76
PBE $\alpha = 0.3, \beta = 0.7$	TBPe	1.57	0.07	-0.19
	TTPA	1.19	-0.04	-0.10
	Terrylene	1.42	0.05	-0.21
	TBRb	1.50	0.00	-0.78
PBE $\alpha = 0.4, \beta = 0.6$	TBPe	1.63	0.11	-0.15
	TTPA	1.35	-0.06	-0.11
	Terrylene	1.46	0.08	-0.18
	TBRb	1.57	0.04	-0.80

Table S8. The computed values of the singlet-triplet energy gaps (eV) using the TPSS-based OT-RSHs-PCM for the experimentally known FEs under study.

OT-RSHs-PCM	Emitter	$\Delta E_{S_1T_1}$	$\Delta E_{S_1T_2}$	$\Delta E_{S_1T_3}$
TPSS $\alpha = 0, \beta = 1.0$	TBPe	1.45	-0.02	-0.26
	TTPA	0.89	-0.03	-0.10
	Terrylene	1.33	0.00	-0.25
	TBRb	1.37	-0.05	-0.74
TPSS $\alpha = 0.1, \beta = 0.9$	TBPe	1.50	0.01	-0.24
	TTPA	1.00	-0.03	-0.10
	Terrylene	1.36	0.02	-0.23
	TBRb	1.42	-0.03	-0.76
TPSS $\alpha = 0.2, \beta = 0.8$	TBPe	1.54	0.04	-0.21
	TTPA	1.12	-0.04	-0.10
	Terrylene	1.40	0.04	-0.21
	TBRb	1.48	0.00	-0.78
TPSS $\alpha = 0.3, \beta = 0.7$	TBPe	1.59	0.08	-0.18
	TTPA	1.25	-0.05	-0.11
	Terrylene	1.44	0.07	-0.20
	TBRb	1.53	0.02	-0.80
TPSS $\alpha = 0.4, \beta = 0.6$	TBPe	1.65	0.12	-0.14
	TTPA	1.40	-0.06	-0.12
	Terrylene	1.48	0.10	-0.17
	TBRb	1.60	0.06	-0.81

Table S9. The computed values of the singlet-triplet energy gaps within the framework of the OT-RSHs-PCM based on the BLYP DFA for different combinations of α and β parameters alongside the corresponding reference experimental data (eV) for the benchmarked set of TADF molecules.

Molecule	$\alpha = 0.0,$ $\beta = 1.0$	$\alpha = 0.1,$ $\beta = 0.9$	$\alpha = 0.2,$ $\beta = 0.8$	$\alpha = 0.3,$ $\beta = 0.7$	Ref.
2CzPN[a]	0.42	0.44	0.48	0.54	0.31
4CzIPN[a]	0.12	0.13	0.14	0.16	0.10
4CzPN[a]	0.12	0.15	0.19	0.25	0.15
4CzTPN[a]	0.14	0.15	0.16	0.17	0.09
ACRFLCN[a]	0.14	0.19	0.27	0.38	0.24
DMAC-DPS[b]	0.02	0.02	0.02	0.02	0.09
DMOC-DPS[c]	0.61	0.64	0.65	0.69	0.24
PPZ-DPO[b]	0.03	0.04	0.06	0.12	0.09
PXZ-DPS[b]	0.05	0.07	0.13	0.26	0.08
PXZ-TRZ[a]	0.01	0.01	0.05	0.10	0.06

[a] S. Huang, Q. Zhang, Y. Shiota, T. Nakagawa, K. Kuwabara, K. Yoshizawa and C. Adachi, Computational Prediction for Singlet- and Triplet-Transition Energies of Charge-Transfer Compounds, *J. Chem. Theory Comput.*, 2013, **9**, 3872-3877.

[b] Q. Zhang, B. Li, S. Huang, H. Nomura, H. Tanaka and C. Adachi, Efficient Blue Organic Light-Emitting Diodes Employing Thermally Activated Delayed Fluorescence, *Nat. Photonics*, 2014, **8**, 326-332.

[c] S. Wu, M. Aonuma, Q. Zhang, S. Huang, T. Nakagawa, K. Kuwabara and C. Adachi, High-Efficiency Deep-Blue Organic Light-Emitting Diodes Based on a Thermally Activated Delayed Fluorescence Emitter, *J. Mater. Chem. C*, 2014, **2**, 421-424.

Table S10. The computed values of the excitation energies (eV) using the standard LC functionals and other RSHs for the experimentally known FEs under study.

Functionals	Emitter	S_1^{FE}	T_1^{FE}	T_2^{FE}	T_3^{FE}
Standard LC functionals					
LC-BLYP	TBPe	3.33	1.51	3.00	3.28
	TTPA	3.35	1.38	3.30	3.50
	Terrylene	2.61	0.98	2.33	2.63
	TBRb	2.62	0.74	2.33	3.30
LC-PBE	TBPe	3.35	1.49	2.98	3.26
	TTPA	3.34	1.35	3.27	3.58
	Terrylene	2.62	0.96	2.31	2.61
	TBRb	2.63	0.71	2.30	3.31
LC-TPSS	TBPe	3.35	1.47	2.97	3.25
	TTPA	3.36	1.34	3.26	3.46
	Terrylene	2.62	0.95	2.30	2.60
	TBRb	2.63	0.69	2.29	3.31
RSHs					
*ω*B97X-D	TBPe	3.08	1.51	3.01	3.27
	TTPA	2.84	1.41	2.95	2.99
	Terrylene	2.38	0.98	2.34	2.60
	TBRb	2.45	0.84	2.37	3.19
CAM-B3LYP	TBPe	3.05	1.45	2.95	3.21
	TTPA	2.76	1.37	2.83	2.88
	Terrylene	2.36	0.93	2.29	2.55
	TBRb	2.39	0.79	2.32	3.14
M11	TBPe	3.26	1.58	3.08	3.35
	TTPA	3.05	1.44	3.18	3.21
	Terrylene	2.53	1.04	2.41	2.68
	TBRb	2.58	0.86	2.41	3.28

Table S11. The computed values of the excitation energies (eV) using the BLYP-based OT-RSH-PCM ($\alpha = 0.0, \beta = 1.0$) for the theoretically designed emitters.

Molecule	S_1^{FE}	T_1^{FE}	T_2^{FE}	T_2^{FE}
I	2.96	1.48	2.97	3.20
II	2.16	1.37	2.40	2.48
III	2.24	0.99	2.20	2.68
IV	2.13	0.94	2.11	2.45
V	2.24	0.97	2.20	2.88
VI	2.27	0.98	2.23	2.88
VII	2.23	0.99	2.31	2.53
VIII	2.19	0.98	2.30	2.51