Electronic Supplementary Information

on

Enhancing NIR-to-visible photon upconversion in cast solid by introducing bulky substituents in rubrene and by suppressing back energy transfer

by

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Fig. S1. ¹H-NMR spectrum of **DMeORb.**

Fig. S2. ¹³C-NMR spectrum of **DMeORb.**

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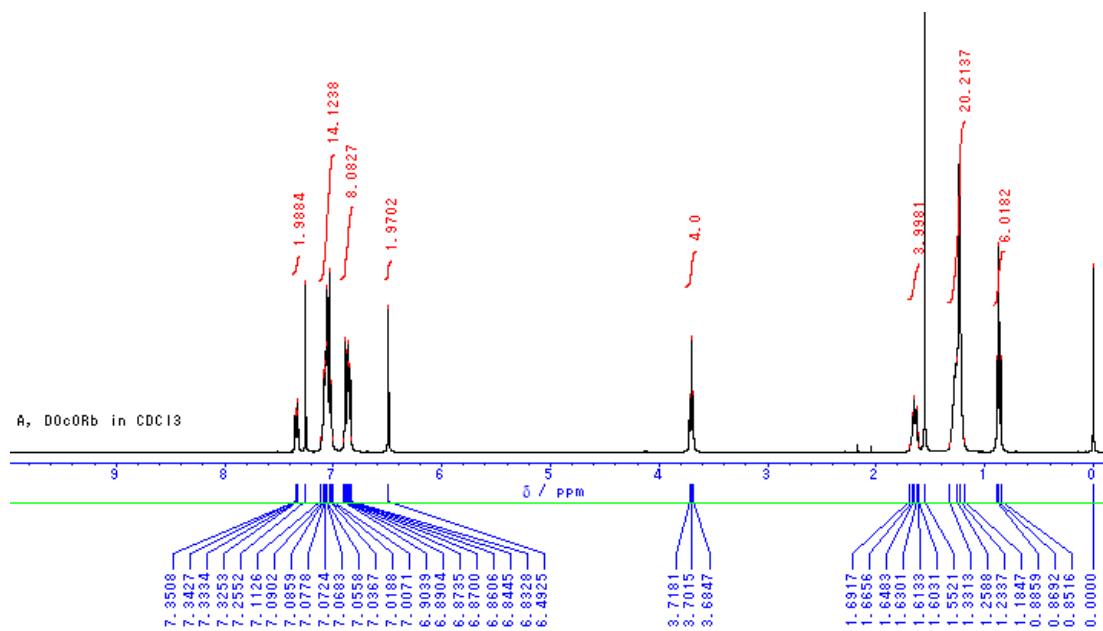
Fig. S3. ^{1}H-NMR spectrum of **DOcORb.**
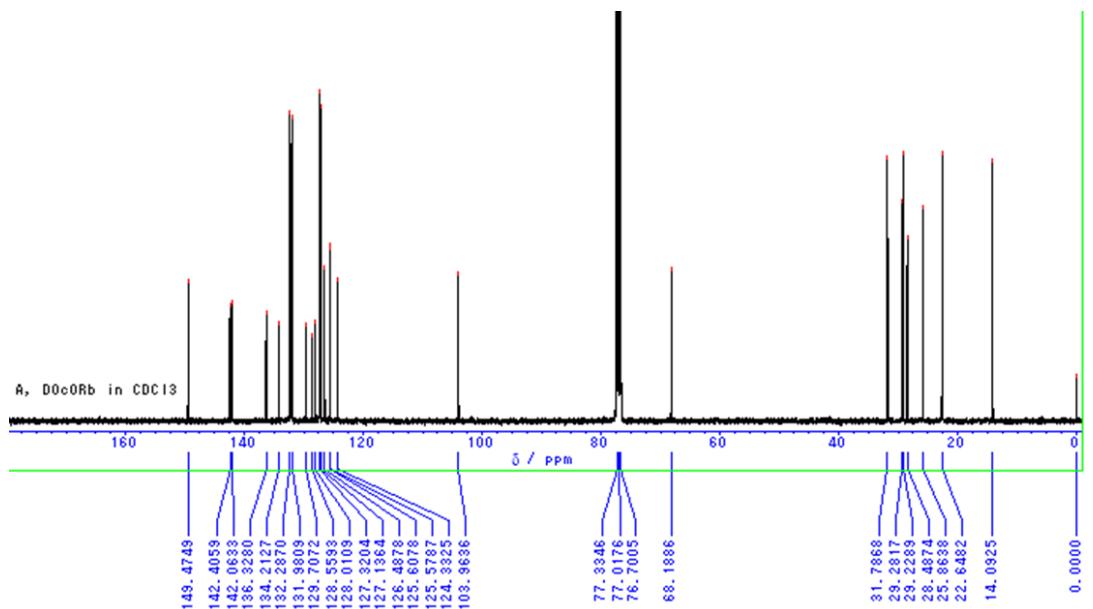
Fig. S4. ^{13}C-NMR spectrum of **DOcORb.**

TBRb

DOcORb

5.5 Å

13 Å

5.0 Å
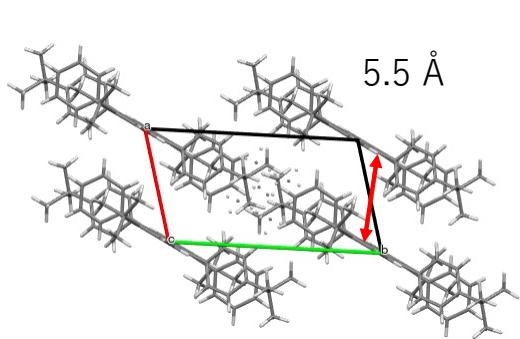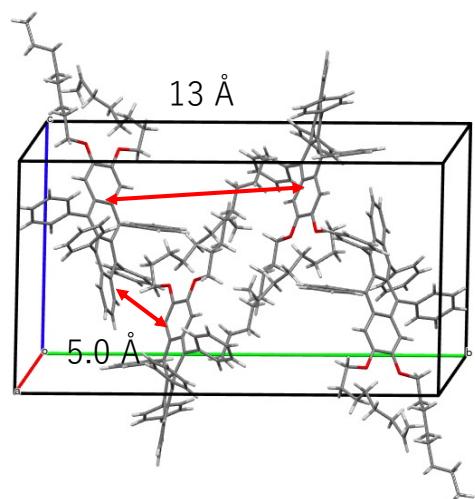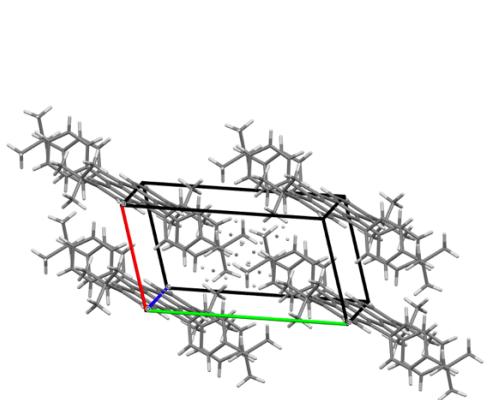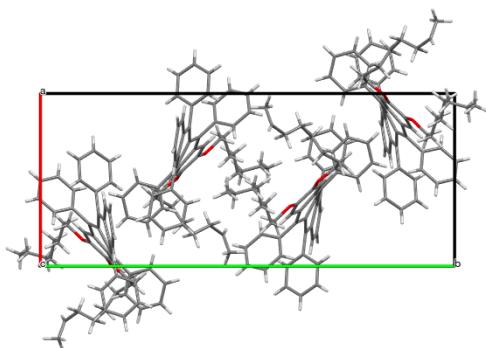
Fig. S5. X-ray crystal structure of **TBRb** and **DOcORb** (only these two of the three derivatives could be defined successfully). *a-, b-,* and *c*-axis are shown in red, green, and blue, respectively (in the top row, *c*-axis is normal to the sheet).

Table S1. Crystallographic data for **TBRb** and **DOcORb**.

Compound	TBRb	DOcORb
empirical formula	$C_{58}H_{60}$	$C_{58}H_{59}O_2$
formula weight	757.06	788.05
T (K)	293(2)	346.15
crystal system	triclinic	monoclinic
space group	P 1	P 1 21/n 1
a (Å)	6.7599(3)	12.0181(5)
b (Å)	12.3329(5)	27.3671(10)
c (Å)	14.0691(4)	14.8672(6)
α (degree)	92.553(3)	90
β (degree)	99.746(3)	108.077(4)
γ (degree)	104.374(3)	90
cell volume ($Å^3$)	1115.20(7)	4648.5(3)
Z	1	4
density (g cm^{-3})	1.127	1.126
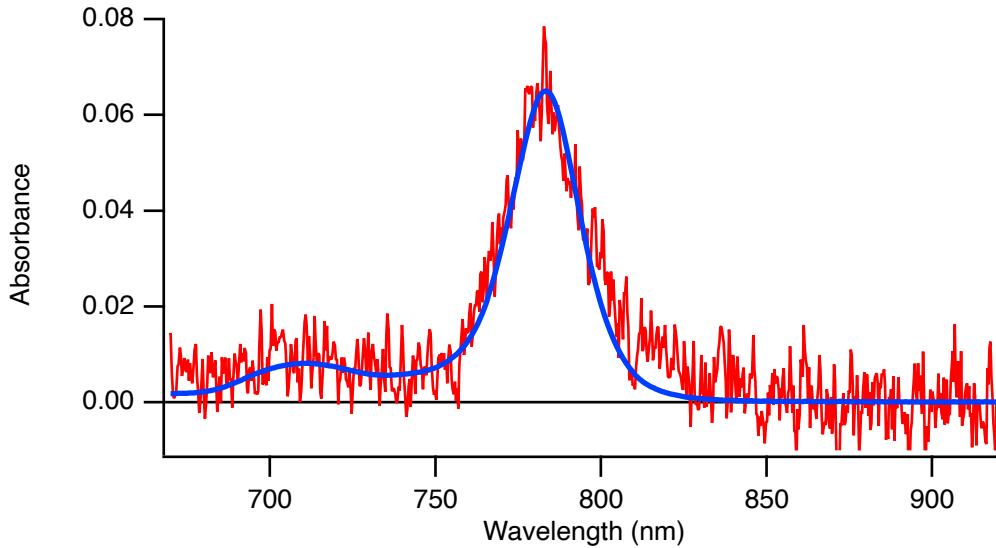
Fig. S6. Example of absorption spectrum of **PdTPTAP:TBRb** cast film (concentration ratio [**PdTPTAP**]:[**TBRb**] = 1:20000) after baseline correction measured by using the microspectroscopic system (red line) together with the solution spectrum of **PdTPTAP** in tetrahydrofuran (blue line). The solution spectrum was scaled to match the film spectrum.
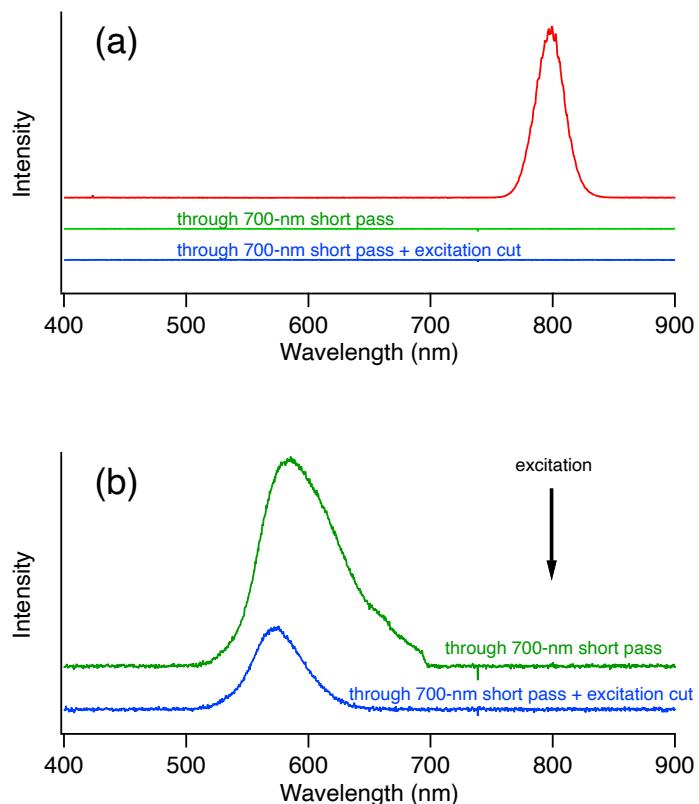
Fig. S7. (a) Spectrum of laser scattering (red) was totally blocked by inserting a 700-nm short-pass filter in the detection path (green), and further added two excitation-cut filters (blue). (b) Emission spectrum of **PdTPTAP:TBRb** film ([sensitizer]:[emitter]=1:2000) through the 700-nm short-pass filter (green) and further added the two excitation-cut filters (blue). The 700-nm short-pass filter (Thorlabs FESH0700) was O.D. >5 at 800 nm and the excitation cut filter (Hoya E-CM500S) was O.D. 3 at 800 nm for a single piece. All data was excited by 800-nm nanosecond laser pulses (10 ns, 1 kHz, 22 kW cm^{-2} at the sample position) and detected by the same detection optics except for the filter combinations. A SMA-connected fiber spectrometer (OceanOptics USB2000) was used instead of the SMA-connected avalanche photodiode used for the time profile measurements by reconnecting a SMA-connecter terminated optical fiber from the detection optics. Spectral correction for the spectrometer was not applied for these data.

(a)

(b)

(c)
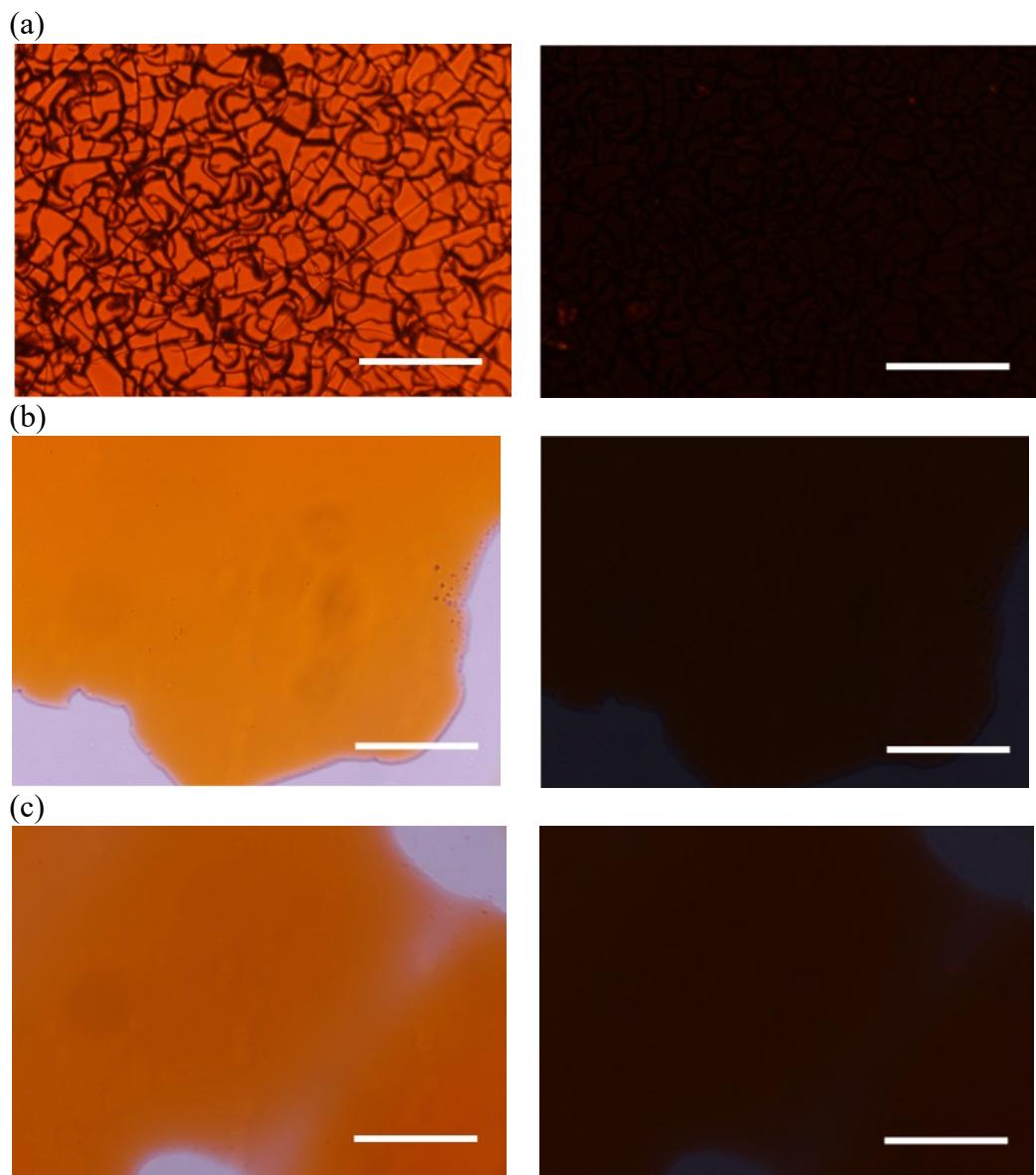
Fig. S8. Parallel polarization (left column) and crossed Nicole (right column) microscopic transmission images of the mixed cast films of the rubrene derivatives: (a) **TBRb**, (b)**DMeORb**, and (c) **DOcORb** with the molar ratio of [sensitizer] : [emitter]=1 : 2000. The bars indicate 100 μm.
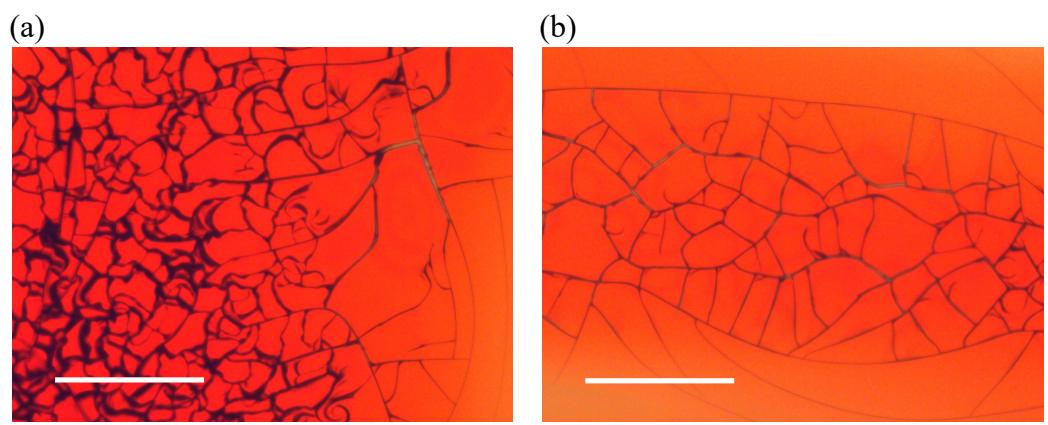
Fig. S9. Microscopic transmission images of the cast films of pristine **TBRb**, at different sample positions ((a) and (b)). The bars indicate 100 μm.
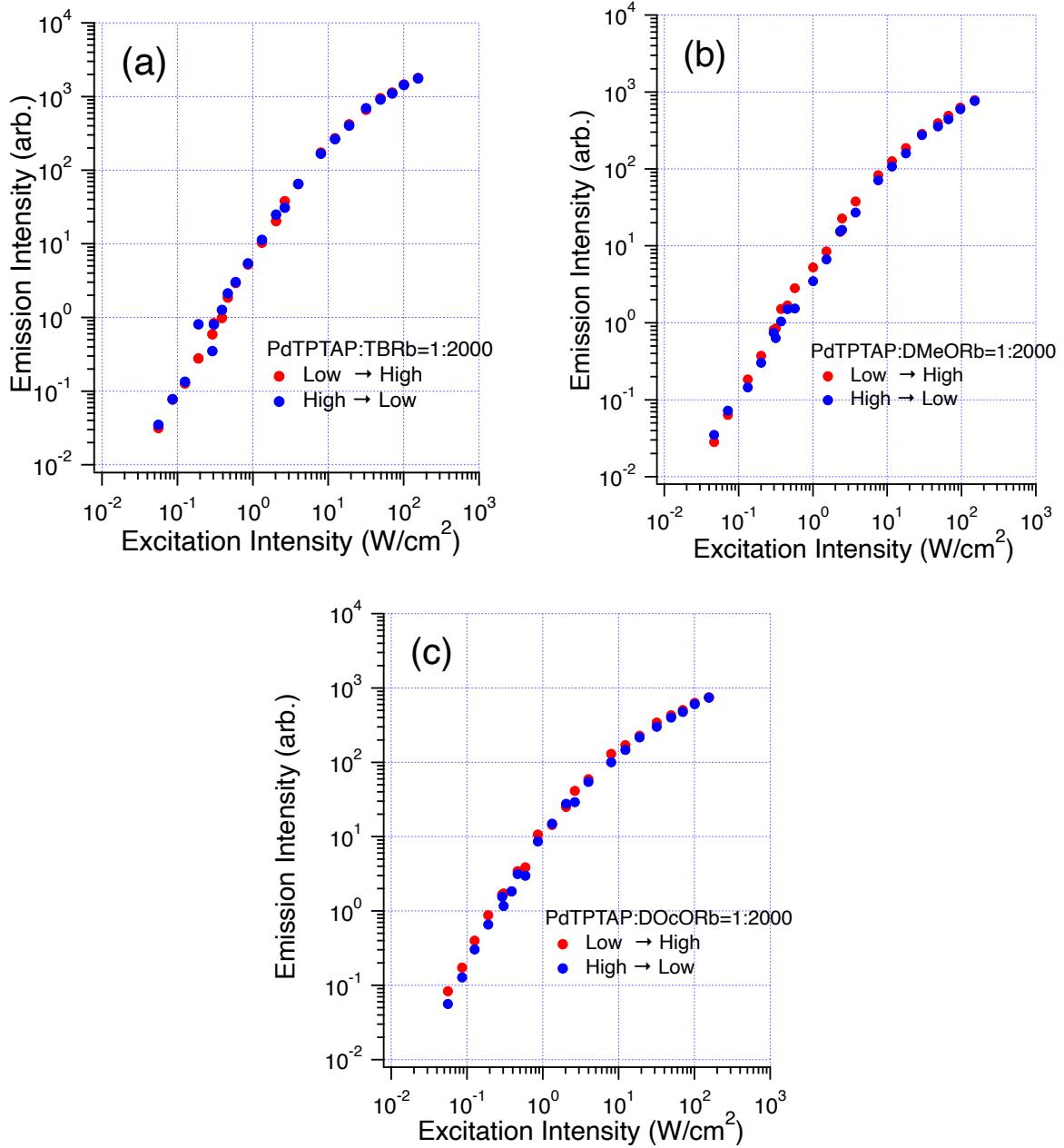
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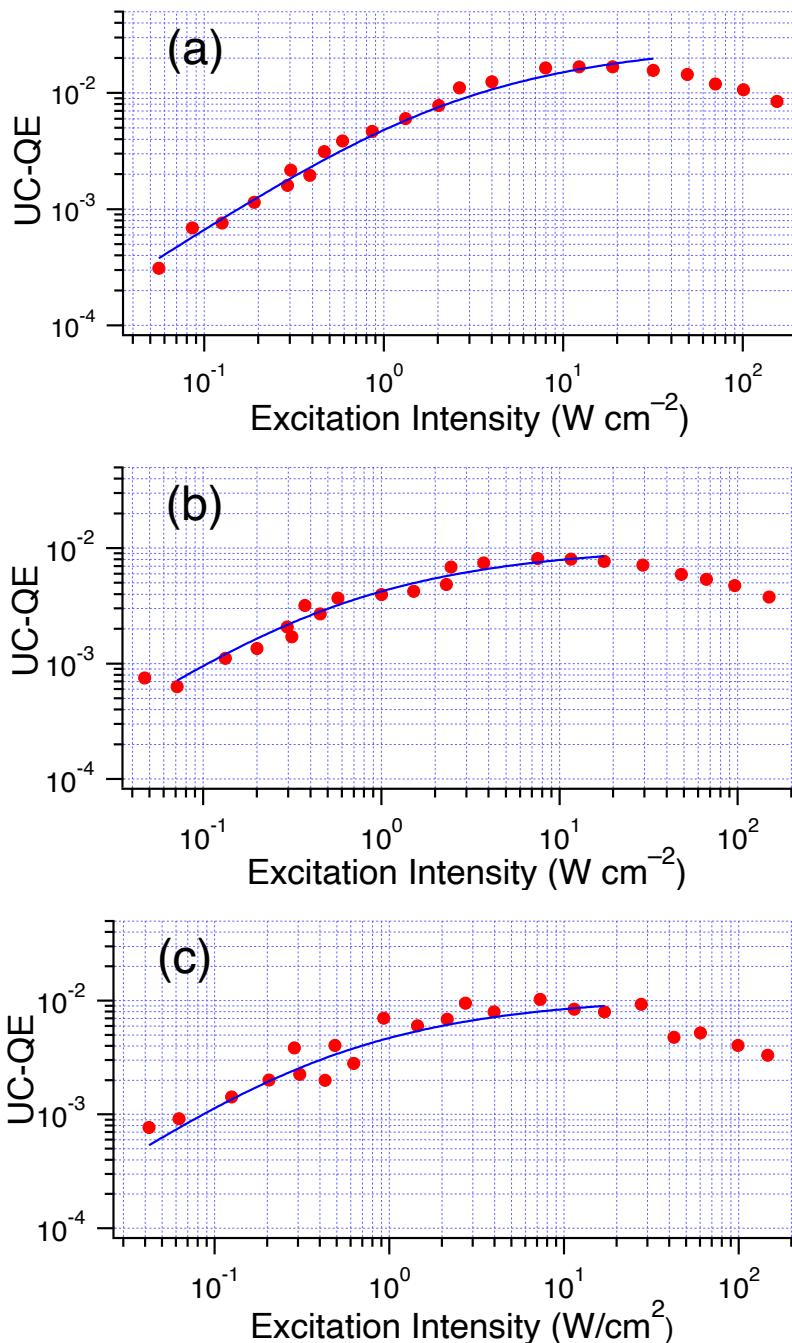
Fig. S11. The excitation intensity dependence of upconversion quantum efficiency η_{UC} of the mixed cast solid films of (a) **PdTPTAP:TBRb**, (b) **PdTPTAP:DMeORb**, and (c) **PdTPTAP: DOcORb**, excited at 785 nm by cw irradiation. The concentration ratio was [**PdTPTAP**]:[**emitter**] = 1:2000 for all. These data were obtained after processing the data in Fig. 4. The solid curves are the curve fits with the theoretical expression, $\eta_{UC} = a\left(1 + \frac{1-\sqrt{1+2bx}}{bx}\right)$ where x and b are the same as in eq. 1 in the main text but $a = \eta_{UC}^{\infty}$, the maximum UC efficiency for the strong excitation limit [from Y. Murakami, K. Kamada, *Phys. Chem. Chem. Phys.* **2021,** *23*, 18268].
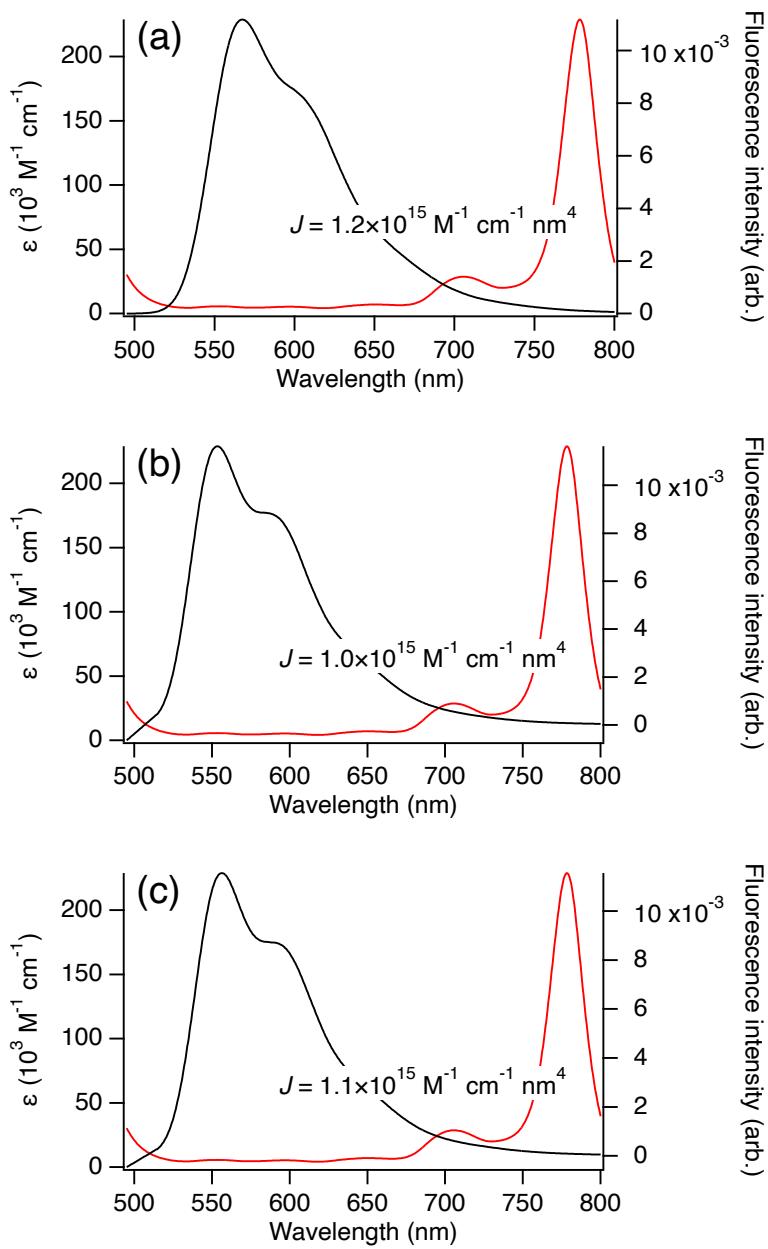
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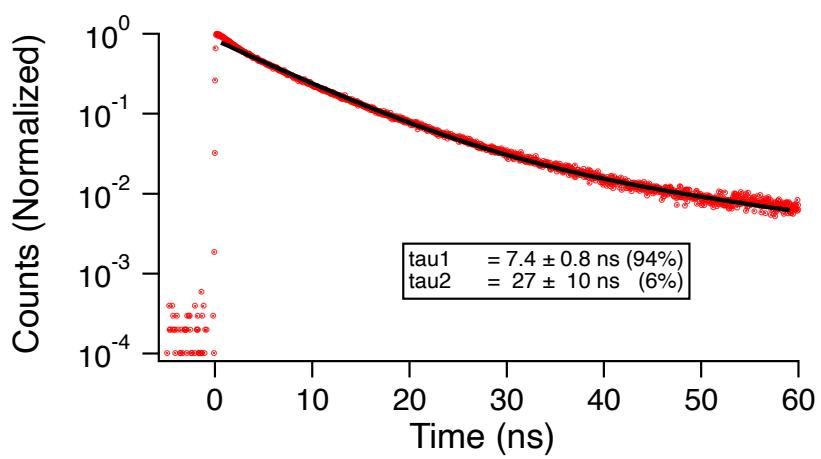
Fig. S13. Prompt fluorescence decay curves of the pristine (pure) cast solids of **TBRb** (symbol) excited at 520±10 nm with the double-exponential fit (solid line).
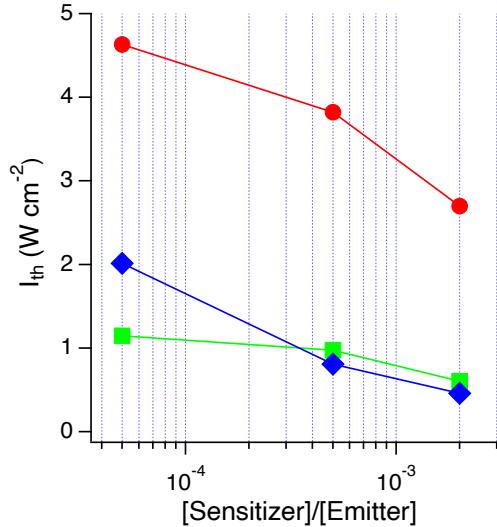
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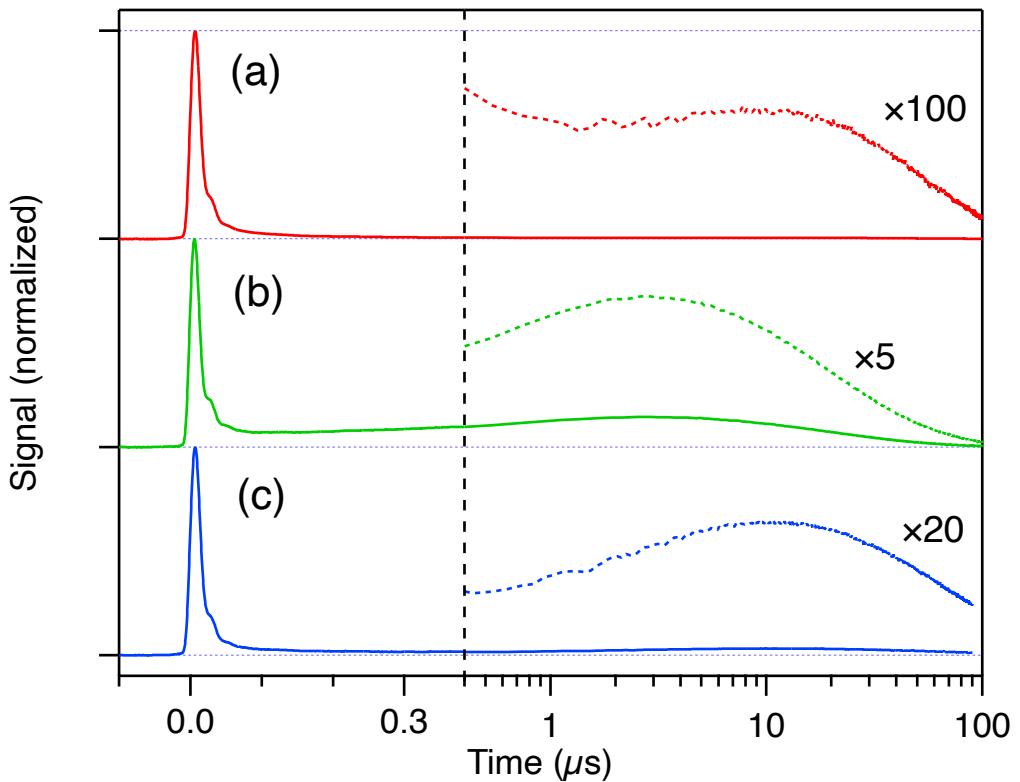
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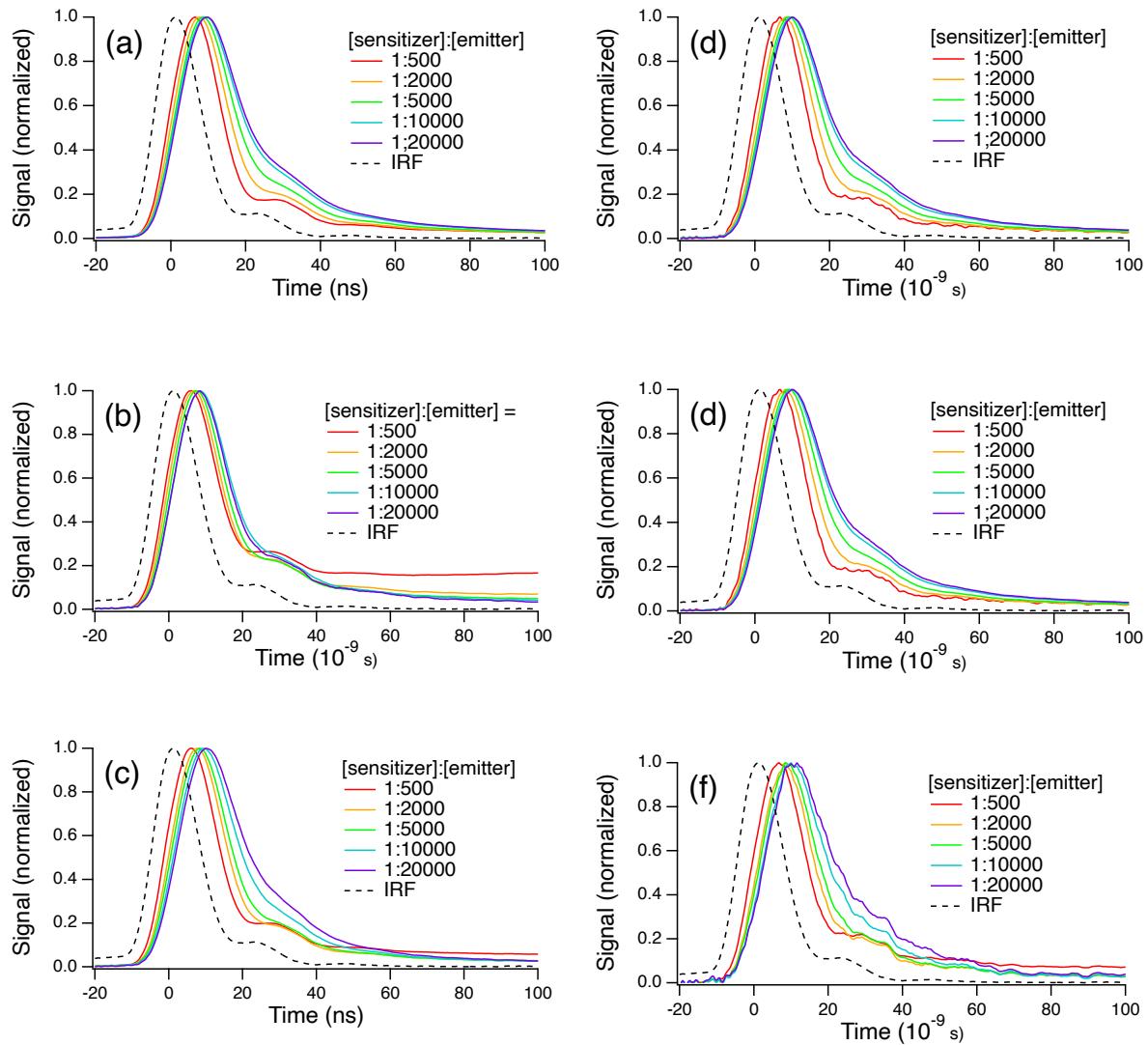
Fig. S16. Nanosecond-scale time profile of upconversion emission of the mixed films of (a),(d) **PdTPTAP:TBRb**, (b),(d) **PdTPTAP:DMeORb**, and (c),(f) **PdTPTAP:DOcORb** with different concentration ratios of the sensitizer and the corresponding emitter as shown in each panel. The samples were excited by nanosecond pulses at 800 nm (10 ns, at 1 kHz repetition) with 22 kW cm^{-2} ((a)-(c)) and 6.5 kW cm^{-2} ((d)–(f)). Emission at the wavelengths shorter than 700 nm was detected through 700-nm short pass and two excitation cut filters.
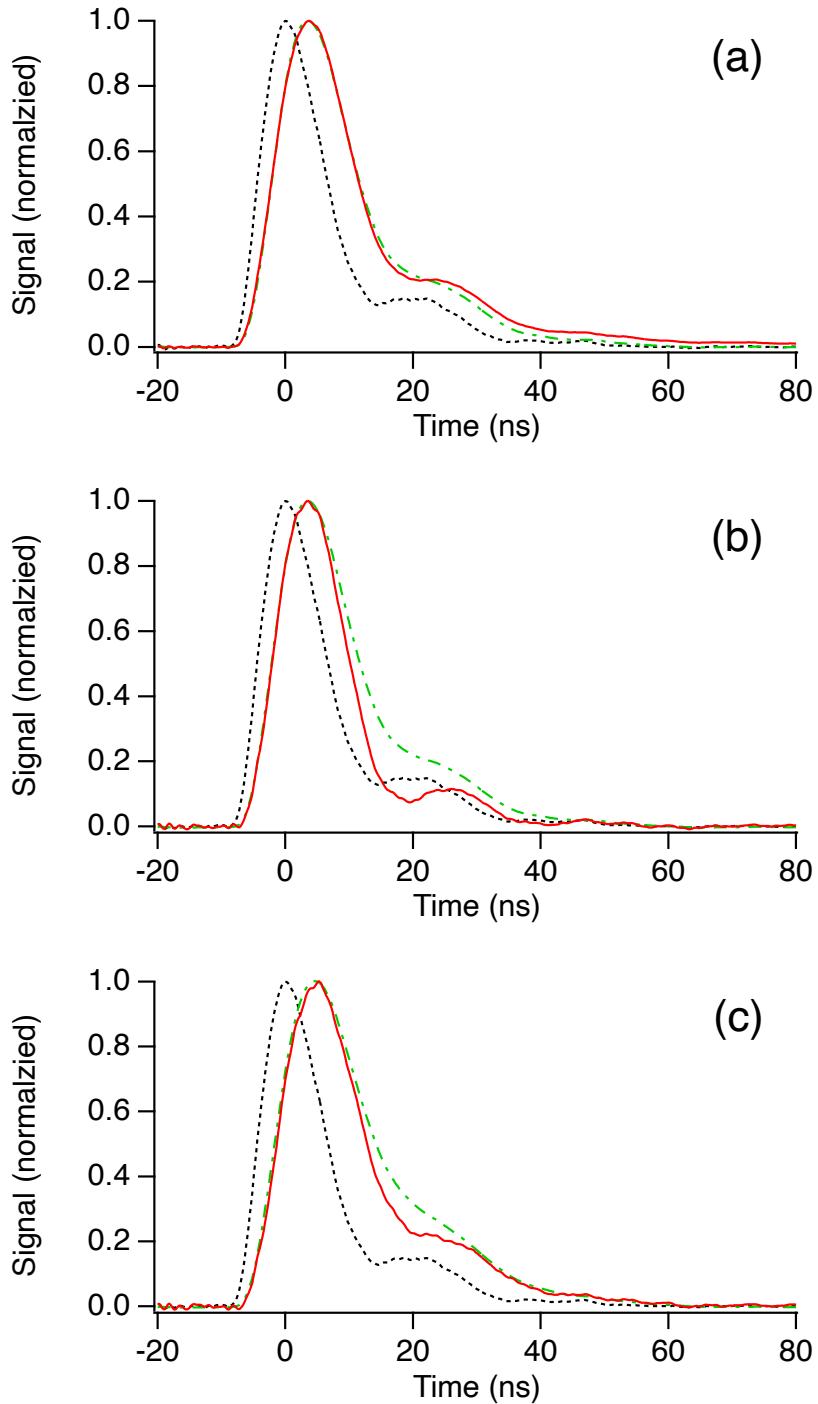
Fig. S17. Time profile of the prompt fluorescence (red solid curve) of the pristine films (no sensitizer) of (a) **TBRb**, (b) **DMeORb**, and (c) **DOcORb** by two-photon excitation with femtosecond laser pulses (800 nm, 120 fs, 4.2 GW cm^{-2}). The results of convolution (green dash-and-dotted curve) of the material response of the exponential decay time constant (τ = (a) 4 ns, (b) 4 ns, (c) 5 ns) with the instrumental response function (black dotted curve) are also presented. The same detection setup was used as for the nanosecond excitation measurements as in Figs. S15 and S16, S18. Emission at the wavelengths shorter than 700 nm was detected.

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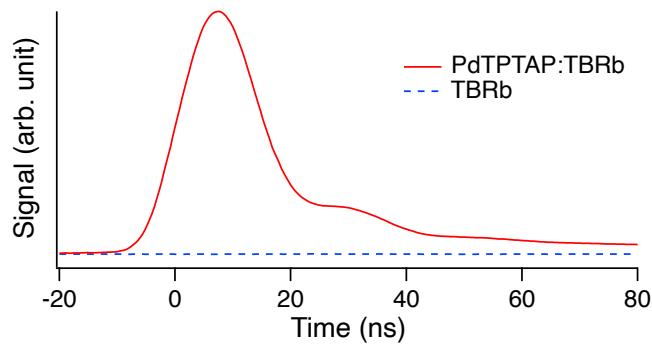
Fig. S18. Emission time profile of **TBRb** cast films without (pristine, blue dashed curve) and with **PdTPTAP** ([sensitizer]:[emitter]=1:1000, red solid curve), both excited by nanosecond laser pulses (10 ns, 1 kHz, 6.5 kW cm^{-2}). Emission at the wavelengths shorter than 700 nm was detected.
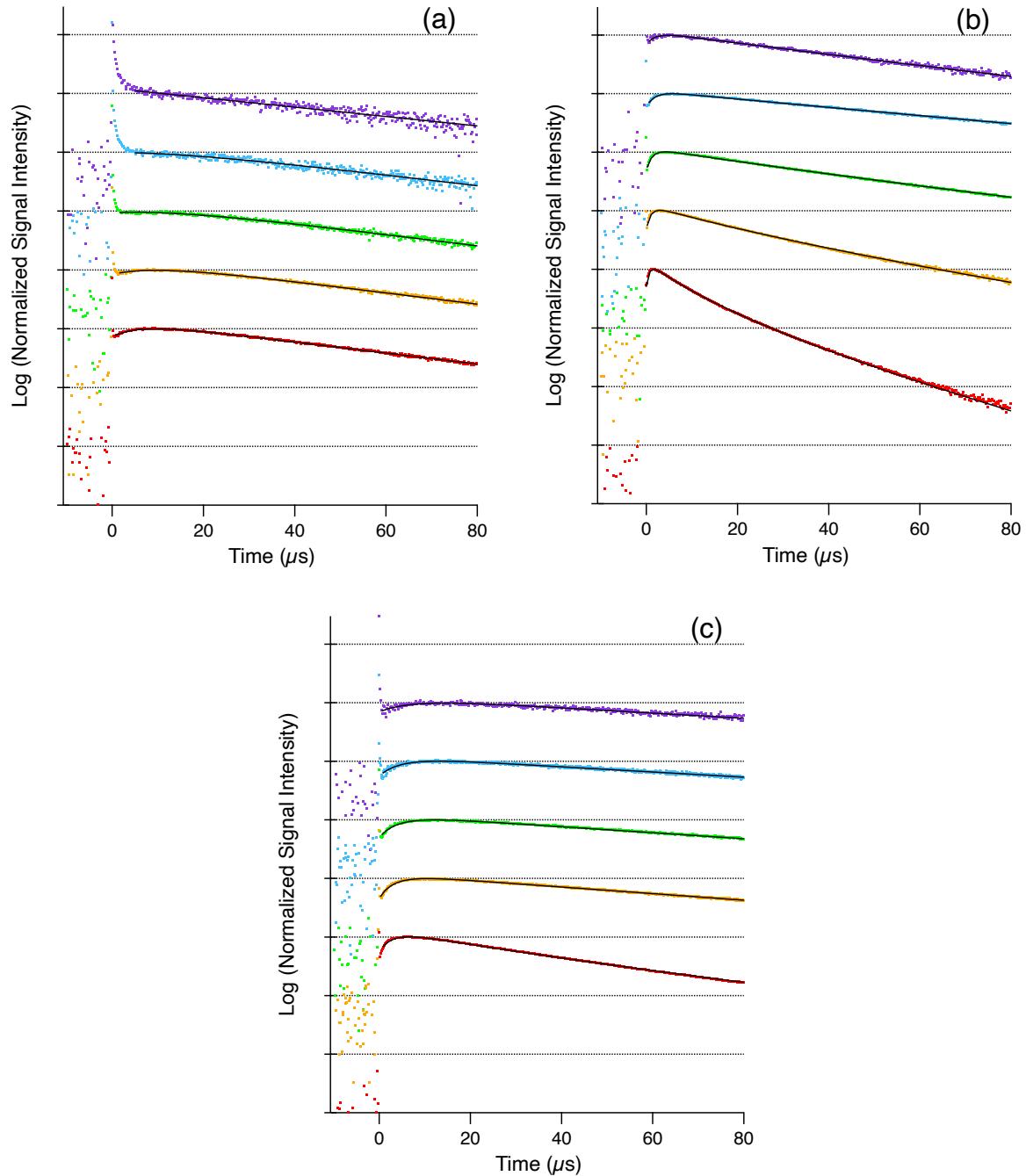
Fig. S19. Semi-log plot of the microsecond-scale time profiles of UC emission of the mixed films of (a) **PdTPTAP:TBRb**, (b) **PdTPTAP:DMeORb**, and (c) **PdTPTAP:DOcORb** with various concentration ratios (from bottom to top, [sensitizer]:[emitter] = 1:500, 1:2000, 1:5000, 1:10000, 1:20000) excited by nanosecond laser pulses (10 ns, 22 kW cm^{-2}). One division of the vertical scale is ten times. Each data was shifted vertically by one division for readability.

Table S2. Best fit parameters to the microsecond-scale emission time profile presented in Fig. S14 by eq. 3.

Emitter [S]:[E]	A	B	τ_R / μs	τ_D / μs	f	τ_{TET}^{slow} / μs	τ_{TET}^{fast} / ns	$\langle \tau_{TET} \rangle$ / μs	Φ_{TET}
TBRb									
1:500	72%	28%	6.6	92.6	0	6.2	40	1.7	90%
1:2000	74%	26%	10.9	90.7	0	9.7	40	2.5	85%
1:5000	78%	22%	17.6	89.5	0	14.7	20	3.2	80%
1:10000	81%	19%	21.6	93.2	0	17.6	40	3.3	80%
1:20000	100%	0%	—	109	0	109	40	0.0	100%
DMeORb									
1:500	64%	36%	0.8	39.4	0.629	0.8	40	0.3	98%
1:2000	62%	38%	1.1	77.3	0.490	1.1	40	0.4	98%
1:5000	65%	35%	1.4	106.8	0.317	1.4	20	0.5	97%
1:10000	72%	28%	2.0	139.6	0.158	2.0	40	0.5	97%
1:20000	78%	22%	0.0	99.7	0.136	2.0	40	0.4	97%
DOeORb									
1:500	64%	36%	3.2	110.9	0.425	3.1	40	1.1	93%
1:2000	62%	38%	3.8	154.3	0.000	3.7	40	1.4	91%
1:5000	64%	36%	4.7	170.3	0.000	4.6	20	1.7	90%
1:10000	68%	32%	5.3	195.8	0.000	5.2	40	1.6	90%
1:20000	75%	25%	0.0	193.6	0.000	7.4	40	1.8	89%
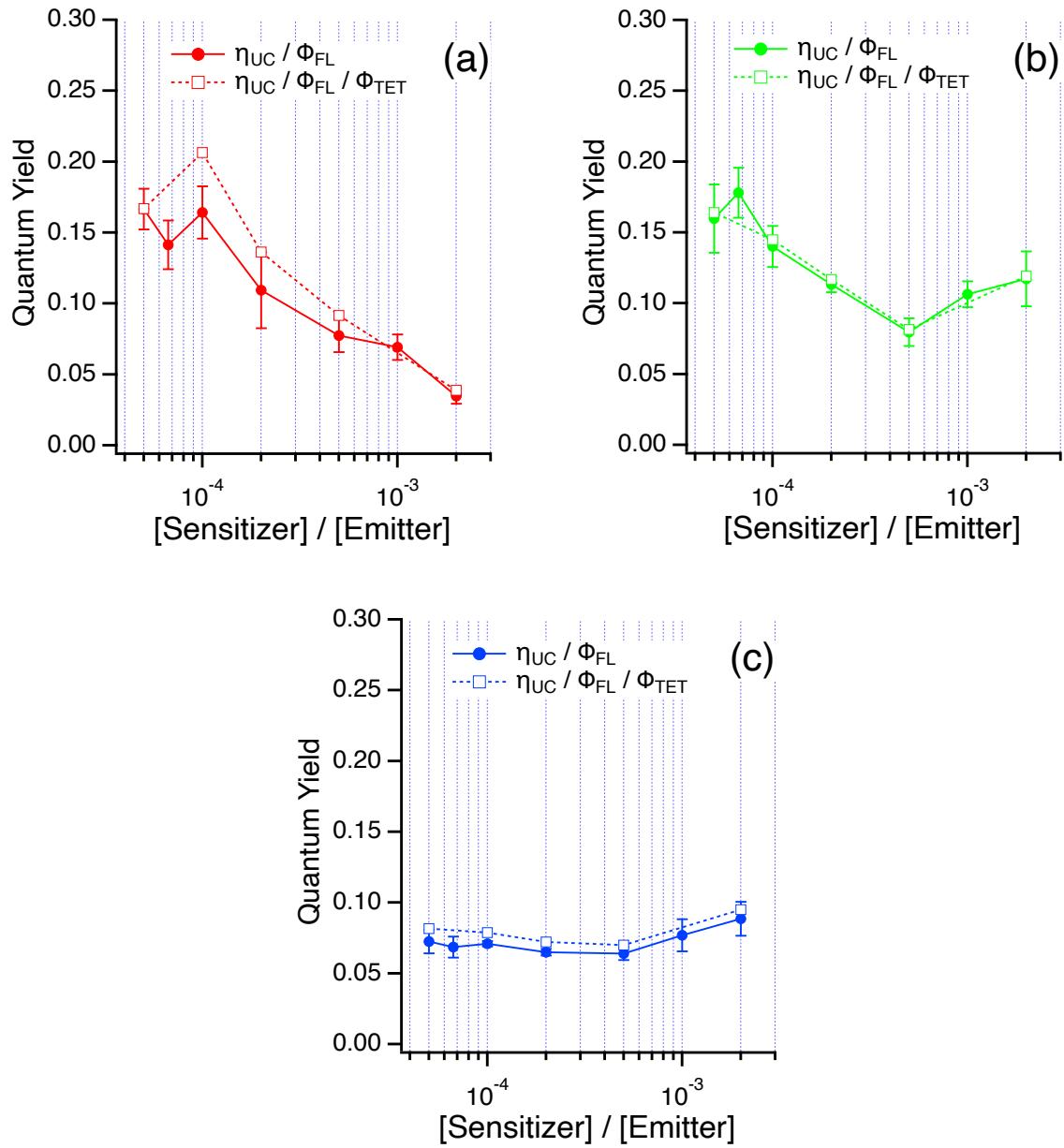
Fig. S20. Plot of the TTA quantum yield calculated by η_{UC} / Φ_{FL} and $\eta_{UC} / (\Phi_{FL}\Phi_{TET})$ of the mixed films of (a) **PdTPTAP:TBRb**, (b) **PdTPTAP:DMeORb**, and (c) **PdTPTAP:DOcORb** with various concentration ratios. The data from Fig. 6 and Table S2 are used.

Table S3.	Optimized geometry of the singlet ground state of rubrene (**Rb**) at B3LYP/6-31G(d).						
C	0.69913	−2.44867	0.19311	C	1.40820	−1.23468	0.25030
C	1.32011	−3.71539	0.47188	C	2.82223	−1.25633	0.74295
C	0.66474	−4.89520	0.25660	C	3.09634	−0.75864	2.02705
C	−0.66477	−4.89520	−0.25661	C	4.38078	−0.83328	2.56571
C	−1.32012	−3.71538	−0.47190	C	5.41744	−1.40671	1.82786
C	−0.69912	−2.44867	−0.19315	C	5.15781	−1.90836	0.55088
C	−1.40818	−1.23466	−0.25033	C	3.87124	−1.84006	0.01697
C	−2.82224	−1.25627	−0.74291	H	2.33716	−3.72565	0.84405
C	−3.09640	−0.75860	−2.02700	H	1.16230	−5.83867	0.46502
C	−4.38087	−0.83320	−2.56559	H	−1.16235	−5.83866	−0.46502
C	−5.41752	−1.40654	−1.82765	H	−2.33717	−3.72563	−0.84408
C	−5.15784	−1.90816	−0.55067	H	−2.28978	−0.31818	−2.60687
C	−3.87123	−1.83991	−0.01684	H	−4.56992	−0.44745	−3.56425
C	−0.72784	−0.00000	−0.00001	H	−6.41958	−1.46448	−2.24454
C	0.72789	−0.00001	−0.00003	H	−5.95894	−2.35400	0.03314
C	1.40821	1.23466	−0.25033	H	−3.67643	−2.22822	0.97845
C	2.82225	1.25630	−0.74297	H	2.28966	0.31861	−2.60710
C	3.09632	0.75889	−2.02718	H	4.56974	0.44800	−3.56458
C	4.38077	0.83355	−2.56582	H	6.41951	1.46469	−2.24477
C	5.41747	1.40671	−1.82783	H	5.95903	2.35377	0.03312
C	5.15789	1.90807	−0.55074	H	3.67657	2.22788	0.97853
C	3.87130	1.83976	−0.01684	H	2.33718	3.72565	−0.84406
C	0.69915	2.44867	−0.19311	H	1.16236	5.83866	−0.46498
C	1.32014	3.71539	−0.47187	H	−1.16229	5.83866	0.46509
C	0.66478	4.89520	−0.25657	H	−2.33713	3.72564	0.84411
C	−0.66472	4.89520	0.25665	H	−2.28972	0.31839	2.60696
C	−1.32008	3.71538	0.47193	H	−4.56985	0.44770	3.56434
C	−0.69910	2.44867	0.19314	H	−6.41955	1.46452	2.24453
C	−1.40816	1.23466	0.25031	H	−5.95896	2.35382	−0.03325
C	−2.82222	1.25628	0.74289	H	−3.67646	2.22801	−0.97856
C	−3.09636	0.75874	2.02705	H	2.28971	−0.31815	2.60685
C	−4.38083	0.83335	2.56563	H	4.56978	−0.44751	3.56437
C	−5.41750	1.40658	1.82764	H	6.41947	−1.46468	2.24481
C	−5.15785	1.90807	0.55061	H	5.95892	−2.35427	−0.03286
C	−3.87124	1.83981	0.01678	H	3.67647	−2.22840	−0.97831

Table S4. Optimized geometry of the triplet ground state of rubrene (**Rb**) at B3LYP/6-31G(d).

C	0.69065	2.48079	−0.19286	C	1.40527	1.22204	−0.27561
C	1.31695	3.71870	−0.44357	C	2.79788	1.22675	−0.81197
C	0.65658	4.92762	−0.23545	C	3.04421	0.64586	−2.06765
C	−0.65663	4.92762	0.23542	C	4.31503	0.68586	−2.64060
C	−1.31699	3.71870	0.44356	C	5.36889	1.30516	−1.96692
C	−0.69068	2.48079	0.19287	C	5.13960	1.88592	−0.71784
C	−1.40529	1.22203	0.27564	C	3.86667	1.85338	−0.15001
C	−2.79789	1.22675	0.81202	H	2.34223	3.73163	−0.79259
C	−3.04420	0.64593	2.06774	H	1.17321	5.86350	−0.43033
C	−4.31501	0.68596	2.64070	H	−1.17327	5.86350	0.43028
C	−5.36889	1.30521	1.96700	H	−2.34227	3.73162	0.79257
C	−5.13962	1.88591	0.71790	H	−2.22515	0.16730	2.59747
C	−3.86669	1.85335	0.15005	H	−4.48004	0.23625	3.61662
C	−0.73480	−0.00000	0.00002	H	−6.36046	1.33572	2.41089
C	0.73478	0.00000	0.00002	H	−5.95498	2.36402	0.18118
C	1.40528	−1.22203	0.27562	H	−3.69957	2.29869	−0.82617
C	2.79789	−1.22674	0.81198	H	2.22519	−0.16724	2.59741
C	3.04423	−0.64588	2.06767	H	4.48010	−0.23613	3.61651
C	4.31506	−0.68588	2.64061	H	6.36050	−1.33563	2.41076
C	5.36892	−1.30514	1.96690	H	5.95498	−2.36399	0.18109
C	5.13962	−1.88588	0.71781	H	3.69954	−2.29870	−0.82621
C	3.86668	−1.85334	0.14999	H	2.34226	−3.73164	0.79256
C	0.69067	−2.48079	0.19286	H	1.17324	−5.86351	0.43028
C	1.31697	−3.71870	0.44355	H	−1.17324	−5.86350	−0.43032
C	0.65660	−4.92763	0.23541	H	−2.34226	−3.73162	−0.79257
C	−0.65660	−4.92762	−0.23545	H	−2.22520	−0.16704	−2.59730
C	−1.31697	−3.71870	−0.44357	H	−4.48008	−0.23597	−3.61646
C	−0.69066	−2.48079	−0.19287	H	−6.36044	−1.33571	−2.41088
C	−1.40528	−1.22204	−0.27561	H	−5.95491	−2.36431	−0.18133
C	−2.79788	−1.22677	−0.81200	H	−3.69950	−2.29898	0.82604
C	−3.04422	−0.64579	−2.06764	H	2.22518	0.16719	−2.59737
C	−4.31503	−0.68581	−2.64061	H	4.48008	0.23609	−3.61649
C	−5.36887	−1.30521	−1.96700	H	6.36047	1.33564	−2.41079
C	−5.13957	−1.88608	−0.71797	H	5.95495	2.36406	−0.18114
C	−3.86665	−1.85352	−0.15011	H	3.69953	2.29876	0.82618

Table S5. Optimized geometry of the singlet ground state of **TBRb** at B3LYP/6-31G(d).

Atom	X	Y	Z	Atom	X	Y	Z
C	−0.64194	−2.46546	−0.51787	H	2.24813	3.74543	−1.18263
C	−1.23493	−3.74435	−0.80720	H	2.30387	0.37249	−2.91699
C	−0.57995	−4.93290	−0.61011	H	4.58573	0.56631	−3.86017
C	0.75639	−4.87518	−0.08715	H	6.39692	1.63793	−2.53023
C	1.39020	−3.68784	0.13605	H	5.89600	2.51463	−0.25532
C	0.75252	−2.42931	−0.13416	H	3.61290	2.31794	0.67716
C	1.43560	−1.20211	−0.06918	H	−2.30383	−0.37247	−2.91701
C	2.84710	−1.19714	0.42732	H	−4.58567	−0.56626	−3.86025
C	3.11881	−0.69147	1.70865	H	−6.39691	−1.63787	−2.53035
C	4.40124	−0.74467	2.24622	H	−5.89605	−2.51457	−0.25543
C	5.47762	−1.30135	1.53485	H	−3.61297	−2.31791	0.67711
C	5.19834	−1.80896	0.25884	C	−2.63537	−6.18154	−1.47928
C	3.91188	−1.76469	−0.28109	C	−1.28066	−7.13091	0.39665
C	0.72780	0.01796	−0.31778	C	−0.33879	−7.05281	−1.94415
C	−0.72782	−0.01796	−0.31777	H	−1.90481	−6.62913	1.14488
C	−1.43563	1.20212	−0.06919	H	−0.29073	−7.28739	0.83815
C	−2.84712	1.19713	0.42734	H	−1.71535	−8.11821	0.19742
C	−3.11877	0.69163	1.70875	H	−3.31519	−5.68332	−0.77921
C	−4.40120	0.74484	2.24634	H	−3.03883	−7.18088	−1.67895
C	−5.47763	1.30132	1.53490	H	−2.64963	−5.62311	−2.42189
C	−5.19841	1.80874	0.25880	C	2.63540	6.18153	−1.47924
C	−3.91195	1.76447	−0.28114	C	1.28069	7.13089	0.39670
C	−0.75255	2.42932	−0.13418	C	0.33882	7.05283	−1.94410
C	−1.39020	3.68785	0.13605	H	0.28312	6.49447	−2.88553
C	−0.75638	4.87519	−0.08714	H	0.76748	8.03961	−2.15842
C	0.57996	4.93290	−0.61009	H	−0.68450	7.20604	−1.58550
C	1.23492	3.74435	−0.80720	H	1.90484	6.62910	1.14492
C	0.64192	2.46546	−0.51788	H	0.29077	7.28738	0.83819
C	1.38042	1.26813	−0.56636	H	1.71540	8.11819	0.19747
C	2.79738	1.32331	−1.04951	H	3.31521	5.68329	−0.77918
C	3.09421	0.83516	−2.33207	H	3.03887	7.18086	−1.67890
C	4.37959	0.94644	−2.86271	H	2.64965	5.62311	−2.42186
C	5.39477	1.54954	−2.11882	H	−0.28308	−6.49444	−2.88556
C	5.11263	2.04257	−0.84301	H	−0.76743	−8.03959	−2.15848
C	3.82548	1.93524	−0.31660	H	0.68454	−7.20601	−1.58554
C	−1.38045	−1.26813	−0.56636	C	7.92624	−1.97822	1.22964
C	−2.79739	−1.32330	−1.04954	C	6.84526	−2.14419	3.47757
C	−3.09419	−0.83513	−2.33210	C	7.34114	0.11415	2.46534
C	−4.37955	−0.94640	−2.86278	H	7.67542	−3.01926	0.99619
C	−5.39476	−1.54948	−2.11892	H	8.90792	−1.97664	1.71690
C	−5.11266	−2.04252	−0.84310	H	8.02464	−1.43023	0.28571
C	−3.82552	−1.93521	−0.31666	H	7.37593	0.71251	1.54773
H	−2.24813	−3.74544	−1.18264	H	8.34356	0.11311	2.91116
C	−1.21030	−6.30172	−0.90857	H	6.66541	0.61614	3.16575
H	1.28817	−5.79829	0.12552	H	6.53236	−3.17790	3.29097
H	2.40642	−3.68782	0.51120	H	6.14940	−1.71122	4.20378
H	2.30929	−0.25890	2.29073	H	7.83928	−2.16806	3.94118
H	4.56092	−0.34517	3.24440	C	−7.92630	1.97797	1.22963
C	6.88318	−1.33215	2.16112	C	−6.84529	2.14439	3.47751
H	5.98909	−2.24847	−0.33916	C	−7.34103	−0.11416	2.46566
H	3.73720	−2.16452	−1.27581	H	−7.67556	3.01899	0.99600
H	−2.30921	0.25921	2.29089	H	−8.90797	1.97639	1.71690
H	−4.56083	0.34549	3.24458	H	−8.02468	1.42982	0.28578
C	−6.88318	1.33213	2.16119	H	−6.53247	3.17809	3.29073
H	−5.98919	2.24809	−0.33926	H	−6.14938	1.71158	4.20377
H	−3.73733	2.16416	−1.27593	H	−7.83930	2.16826	3.94113
H	−2.40642	3.68785	0.51122	H	−7.37580	−0.71267	1.54814
H	−1.28815	5.79831	0.12555	H	−8.34344	−0.11311	2.91150
C	1.21033	6.30172	−0.90854	H	−6.66525	−0.61599	3.16614

Table S6. Optimized geometry of the triplet ground state of **TBRb** at B3LYP/6-31G(d).

Atom	x	y	z	Atom	x	y	z
C	0.78101	2.45292	-0.56433	H	-2.47402	-3.60577	-1.18252
C	1.45469	3.66402	-0.82876	H	-2.23475	-0.04983	-2.94244
C	0.86933	4.91994	-0.63919	H	-4.49163	-0.01859	-3.95843
C	-0.44957	4.94367	-0.15577	H	-6.41012	-1.06848	-2.76800
C	-1.15969	3.76990	0.06627	H	-6.03972	-2.14645	-0.55518
C	-0.59463	2.50197	-0.17565	H	-3.78327	-2.17334	0.45219
C	-1.35741	1.27437	-0.08057	H	2.23484	0.04979	-2.94236
C	-2.74130	1.32958	0.46961	H	4.49179	0.01848	-3.95819
C	-3.01131	0.72893	1.71132	H	6.41024	1.06832	-2.76763
C	-4.27283	0.80861	2.29198	H	6.03971	2.14628	-0.55482
C	-5.33350	1.48558	1.66606	H	3.78319	2.17324	0.45238
C	-5.05910	2.08357	0.42871	C	3.03577	6.00715	-1.46460
C	-3.79282	2.01432	-0.15388	C	1.72001	7.05747	0.38506
C	-0.73406	0.02688	-0.35879	C	0.82463	7.05491	-1.97430
C	0.73401	-0.02690	-0.35878	H	2.28247	6.50651	1.14752
C	1.35736	-1.27439	-0.08054	H	0.73488	7.29214	0.80176
C	2.74127	-1.32958	0.46962	H	2.23847	8.00627	0.19892
C	3.01130	-0.72890	1.71130	H	3.66276	5.46110	-0.75091
C	4.27283	-0.80854	2.29194	H	3.51721	6.97302	-1.65588
C	5.33350	-1.48550	1.66600	H	3.02811	5.44818	-2.40702
C	5.05908	-2.08352	0.42867	C	-3.03576	-6.00718	-1.46467
C	3.79279	-2.01430	-0.15389	C	-1.72005	-7.05750	0.38501
C	0.59459	-2.50200	-0.17562	C	-0.82461	-7.05494	-1.97433
C	1.15965	-3.76992	0.06630	H	-0.73998	-6.50195	-2.91678
C	0.44955	-4.94370	-0.15576	H	-1.33563	-8.00348	-2.18106
C	-0.86934	-4.91997	-0.63921	H	0.18893	-7.28999	-1.63294
C	-1.45471	-3.66405	-0.82879	H	-2.28252	-6.50655	1.14746
C	-0.78104	-2.45295	-0.56434	H	-0.73493	-7.29217	0.80174
C	-1.45059	-1.16772	-0.63801	H	-2.23849	-8.00631	0.19886
C	-2.84330	-1.11383	-1.17215	H	-3.66277	-5.46114	-0.75100
C	-3.07031	-0.50569	-2.41861	H	-3.51719	-6.97306	-1.65597
C	-4.34240	-0.48946	-2.98996	H	-3.02808	-5.44821	-2.40709
C	-5.41784	-1.08020	-2.32472	H	0.74003	6.50193	-2.91675
C	-5.20845	-1.68778	-1.08487	H	1.33567	8.00346	-2.18102
C	-3.93464	-1.70925	-0.51778	H	-0.18891	7.28997	-1.63293
C	1.45056	1.16769	-0.63798	C	-7.74435	2.32593	1.49948
C	2.84330	1.11377	-1.17203	C	-6.59600	2.22795	3.71782
C	3.07038	0.50563	-2.41847	C	-7.25214	0.10103	2.52747
C	4.34251	0.48936	-2.98973	H	-7.43691	3.36705	1.34872
C	5.41792	1.08007	-2.32441	H	-8.71047	2.33864	2.01677
C	5.20846	1.68765	-1.08458	H	-7.90222	1.87004	0.51548
C	3.93461	1.70915	-0.51757	H	-7.34692	-0.41009	1.56253
H	2.47401	3.60574	-1.18246	H	-8.24048	0.11910	3.00336
C	1.61225	6.23684	-0.92272	H	-6.58886	-0.49900	3.15928
H	-0.94287	5.89145	0.04122	H	-6.22789	3.25495	3.61284
H	-2.18071	3.83616	0.42237	H	-5.90755	1.69320	4.38048
H	-2.21466	0.19999	2.22741	H	-7.57405	2.26607	4.21335
H	-4.42881	0.33289	3.25680	C	7.74436	-2.32580	1.49938
C	-6.71733	1.54052	2.33696	C	6.59606	-2.22779	3.71775
H	-5.83962	2.61273	-0.10697	C	7.25213	-0.10089	2.52733
H	-3.62725	2.47960	-1.12123	H	7.43695	-3.36693	1.34865
H	2.21465	-0.19995	2.22740	H	8.71050	-2.33848	2.01664
H	4.42882	-0.33279	3.25674	H	7.90220	-1.86993	0.51537
C	6.71734	-1.54039	2.33686	H	6.22798	-3.25481	3.61280
H	5.83960	-2.61267	-0.10701	H	5.90763	-1.69304	4.38042
H	3.62721	-2.47961	-1.12123	H	7.57414	-2.26588	4.21325
H	2.18067	-3.83618	0.42242	H	7.34687	0.41022	1.56237
H	0.94284	-5.89147	0.04123	H	8.24048	-0.11893	3.00320
C	-1.61225	-6.23686	-0.92276	H	6.58885	0.49915	3.15915

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Table S7. Optimized geometry of the singlet ground state of **DMeORb** at B3LYP/6-31G(d).

C	−0.69539	−3.09066	−0.20286	O	1.20251	5.49585	−0.46012
C	−1.31373	−4.35638	−0.48651	H	2.35922	3.07452	−0.77576
C	−0.66147	−5.53746	−0.26327	H	2.34665	−0.26906	−2.56717
C	0.66146	−5.53746	0.26327	H	4.64755	−0.12268	−3.47193
C	1.31372	−4.35638	0.48652	H	6.46896	0.86445	−2.09110
C	0.69538	−3.09066	0.20287	H	5.95914	1.70418	0.19524
C	1.40219	−1.87359	0.27440	H	3.65571	1.55937	1.08769
C	2.80917	−1.89926	0.78740	H	−2.24851	−0.98935	−2.65658
C	3.06443	−1.41987	2.08226	H	−4.51535	−1.12883	−3.64509
C	4.34122	−1.50032	2.63824	H	−6.38523	−2.12509	−2.33804
C	5.38924	−2.06210	1.90742	H	−5.95838	−2.98340	−0.04179
C	5.14847	−2.54616	0.62000	H	−3.68905	−2.84706	0.93412
C	3.86950	−2.47160	0.06879	C	2.53387	5.57407	−0.94531
C	0.72732	−0.64084	0.01621	C	−2.53385	5.57408	0.94531
C	−0.72732	−0.64084	−0.01621	H	2.74886	6.63844	−1.05490
C	−1.41281	0.59916	0.21164	H	2.63496	5.07592	−1.91833
C	−2.83821	0.62751	0.67256	H	3.24502	5.12636	−0.23894
C	−3.14068	0.15881	1.96114	H	−2.74883	6.63846	1.05491
C	−4.43688	0.24307	2.47001	H	−2.63494	5.07593	1.91833
C	−5.45773	0.79956	1.69792	H	−3.24500	5.12638	0.23895
C	−5.17019	1.27371	0.41628				
C	−3.87208	1.19433	−0.08802				
C	−0.70333	1.80914	0.17209				
C	−1.33357	3.07516	0.43646				
C	−0.68154	4.26077	0.24361				
C	0.68155	4.26076	−0.24361				
C	1.33358	3.07515	−0.43647				
C	0.70334	1.80914	−0.17210				
C	1.41281	0.59916	−0.21164				
C	2.83821	0.62752	−0.67256				
C	3.14070	0.15876	−1.96111				
C	4.43690	0.24301	−2.46999				
C	5.45772	0.79957	−1.69792				
C	5.17017	1.27379	−0.41630				
C	3.87207	1.19441	0.08799				
C	−1.40219	−1.87359	−0.27439				
C	−2.80917	−1.89925	−0.78740				
C	−3.06442	−1.41990	−2.08228				
C	−4.34121	−1.50034	−2.63827				
C	−5.38924	−2.06206	−1.90742				
C	−5.14849	−2.54606	−0.61997				
C	−3.86952	−2.47151	−0.06876				
H	−2.32672	−4.36699	−0.86983				
H	−1.15786	−6.48057	−0.47640				
H	1.15785	−6.48057	0.47640				
H	2.32671	−4.36699	0.86984				
H	2.24853	−0.98926	2.65654				
H	4.51537	−1.12876	3.64505				
H	6.38522	−2.12514	2.33804				
H	5.95834	−2.98356	0.04184				
H	3.68901	−2.84720	−0.93407				
H	−2.34662	−0.26895	2.56722				
H	−4.64753	−0.12258	3.47197				
H	−6.46896	0.86443	2.09110				
H	−5.95917	1.70404	−0.19529				
H	−3.65573	1.55924	−1.08774				
H	−2.35921	3.07454	0.77576				
O	−1.20249	5.49585	0.46012				

Table S8. Optimized geometry of the triplet ground state of **DMeORb** at B3LYP/6-31G(d).

C	0.69095	1.83765	−0.17506	H	2.33468	−4.37582	0.81328
C	1.32641	3.07864	−0.40928	H	1.17000	−6.50814	0.44012
C	0.67300	4.29000	−0.22307	H	−1.16920	−6.50819	−0.44090
C	−0.67346	4.28992	0.22323	H	−2.33411	−4.37592	−0.81369
C	−1.32673	3.07849	0.40947	H	−2.17942	−0.81790	−2.63472
C	−0.69112	1.83757	0.17528	H	−4.41584	−0.89053	−3.69402
C	−1.40883	0.58270	0.24516	H	−6.31796	−1.98526	−2.51800
C	−2.81391	0.59440	0.74958	H	−5.95221	−3.00510	−0.27740
C	−3.08915	0.03255	2.00791	H	−3.71490	−2.93593	0.76957
C	−4.37224	0.08216	2.55218	H	2.28267	−0.44048	−2.56126
C	−5.41027	0.69375	1.84742	H	4.55928	−0.35418	−3.53012
C	−5.15269	1.25595	0.59537	H	6.41106	0.73221	−2.26940
C	−3.86754	1.21246	0.05556	H	5.95567	1.72697	−0.03396
C	−0.73411	−0.64026	−0.01081	H	3.67862	1.64137	0.92425
C	0.73428	−0.64018	0.01103	C	−2.57193	5.57337	0.87741
C	1.40166	−1.86460	0.29389	C	2.57131	5.57367	−0.87726
C	2.78391	−1.86978	0.85571	H	−2.80643	6.63489	0.97568
C	3.00813	−1.29458	2.11833	H	−3.26106	5.11316	0.15702
C	4.26845	−1.33663	2.71386	H	−2.69176	5.08137	1.85157
C	5.33473	−1.95267	2.05667	H	3.26050	5.11355	−0.15687
C	5.12789	−2.52787	0.80115	H	2.80568	6.63521	−0.97555
C	3.86529	−2.49283	0.21070	H	2.69121	5.08166	−1.85141
C	0.68908	−3.12467	0.19944				
C	1.31256	−4.36224	0.45503				
C	0.65428	−5.57266	0.24066				
C	−0.65357	−5.57269	−0.24130				
C	−1.31198	−4.36230	−0.45546				
C	−0.68862	−3.12471	−0.19968				
C	−1.40135	−1.86471	−0.29385				
C	−2.78364	−1.86993	−0.85559				
C	−3.00811	−1.29406	−2.11785				
C	−4.26848	−1.33605	−2.71327				
C	−5.33455	−1.95272	−2.05635				
C	−5.12747	−2.52860	−0.80118				
C	−3.86482	−2.49359	−0.21082				
C	1.40884	0.58289	−0.24494				
C	2.81384	0.59481	−0.74957				
C	3.08905	0.03267	−2.00778				
C	4.37204	0.08250	−2.55226				
C	5.40999	0.69461	−1.84786				
C	5.15244	1.25714	−0.59594				
C	3.86739	1.21342	−0.05591				
H	2.35846	3.07960	−0.72977				
O	1.22799	5.51585	−0.42527				
O	−1.22860	5.51571	0.42541				
H	−2.35877	3.07933	0.72997				
H	−2.28273	−0.44020	2.56166				
H	−4.55951	−0.35427	3.53015				
H	−6.41142	0.73118	2.26879				
H	−5.95597	1.72535	0.03311				
H	−3.67875	1.64014	−0.92472				
H	2.17928	−0.81892	2.63540				
H	4.41561	−0.89165	3.69488				
H	6.31810	−1.98526	2.51840				
H	5.95279	−3.00389	0.27718				
H	3.71557	−2.93465	−0.76995				

Table S9. Optimized geometry of the singlet ground state of the model of **DOcORb** (each octyl group is replaced with ethyl group) at B3LYP/6-31G(d).

C	3.44543	−0.69309	−0.21368	H	−1.20166	−3.63404	−1.15635
C	4.71105	−1.30756	−0.50616	H	−2.72070	−2.37197	0.73280
C	5.89235	−0.65927	−0.27291	O	−5.14186	−1.21011	0.43642
C	5.89273	0.65594	0.27286	O	−5.14115	1.21299	−0.43673
C	4.71181	1.30489	0.50616	H	−2.71929	2.37348	−0.73294
C	3.44583	0.69114	0.21374	H	0.61462	2.39251	−2.52869
C	2.22890	1.39694	0.29682	H	0.46211	4.70935	−3.39204
C	2.25603	2.79490	0.83435	H	−0.52087	6.50477	−1.97478
C	1.78092	3.02699	2.13511	H	−1.35071	5.95350	0.30552
C	1.86467	4.29322	2.71439	H	−1.20019	3.63468	1.15605
C	2.42549	5.35385	2.00126	H	1.34903	−2.20184	−2.69485
C	2.90524	5.13611	0.70808	H	1.49313	−4.44999	−3.72507
C	2.82740	3.86762	0.13365	H	2.48733	−6.34311	−2.44977
C	0.99569	0.72681	0.02839	H	3.33901	−5.95775	−0.14382
C	0.99529	−0.72739	−0.02824	H	3.19899	−3.70679	0.87296
C	−0.24504	−1.41614	0.18684	C	−5.23315	2.56115	−0.89759
C	−0.27547	−2.84968	0.62191	C	−5.23465	−2.55813	0.89752
C	0.18665	−3.17565	1.90712	C	−6.70738	2.89157	−1.05128
C	0.09795	−4.48061	2.39253	H	−4.70188	2.66141	−1.85464
C	−0.45652	−5.48659	1.59979	H	−4.74937	3.23308	−0.17464
C	−0.92437	−5.17558	0.32125	C	−6.70907	−2.88751	1.05170
C	−0.84046	−3.86894	−0.15949	H	−4.70317	−2.65855	1.85443
C	−1.45503	−0.70576	0.15967	H	−4.75155	−3.23055	0.17456
C	−2.72111	−1.34062	0.41197	H	−7.22985	−2.78309	0.09476
C	−3.90719	−0.68525	0.23073	H	−7.18095	−2.21561	1.77537
C	−3.90678	0.68745	−0.23092	H	−6.82873	−3.91805	1.40329
C	−2.72031	1.34214	−0.41208	H	−7.18072	2.21712	−1.77162
C	−1.45462	0.70656	−0.15969	H	−6.82631	3.92073	−1.40712
C	−0.24423	1.41626	−0.18677	H	−7.22729	2.79175	−0.09337
C	−0.27384	2.84980	−0.62190				
C	0.18883	3.17549	−1.90698				
C	0.10093	4.48048	−2.39246				
C	−0.45327	5.48677	−1.59993				
C	−0.92168	5.17603	−0.32152				
C	−0.83857	3.86936	0.15930				
C	2.22810	−1.39821	−0.29671				
C	2.25442	−2.79618	−0.83426				
C	1.77894	−3.02800	−2.13493				
C	1.86191	−4.29426	−2.71425				
C	2.42234	−5.35519	−2.00124				
C	2.90246	−5.13772	−0.70816				
C	2.82539	−3.86920	−0.13370				
H	4.72126	−2.31454	−0.90485				
H	6.83532	−1.15283	−0.49314				
H	6.83599	1.14896	0.49304				
H	4.72261	2.31187	0.90485				
H	1.35070	2.20106	2.69512				
H	1.49616	4.44915	3.72529				
H	2.49108	6.34174	2.44976				
H	3.34210	5.95591	0.14364				
H	3.20071	3.70501	−0.87308				
H	0.61264	−2.39290	2.52898				
H	0.45871	−4.70969	3.39222				
H	−0.52474	−6.50458	1.97459				
H	−1.35359	−5.95282	−0.30594				

Table S10. Optimized geometry of the triplet ground state of the model of **DOcORb** (each octyl group is replaced with ethyl group) at B3LYP/6-31G(d).

C	−3.47866	0.68401	−0.21282	H	2.72438	2.36919	0.69713
C	−4.71651	1.30203	−0.47994	O	5.16086	1.23575	0.40842
C	−5.92665	0.64761	−0.25294	O	5.16161	−1.23260	−0.40856
C	−5.92622	−0.65115	0.25340	H	2.72583	−2.36751	−0.69732
C	−4.71565	−1.30483	0.48025	H	−0.81739	−2.31555	−2.51765
C	−3.47822	−0.68604	0.21298	H	−0.74454	−4.60505	−3.45676
C	−2.21794	−1.39636	0.32063	H	0.35357	−6.44126	−2.18276
C	−2.21818	−2.76517	0.91442	H	1.37246	−5.95691	0.03545
C	−1.63031	−2.95830	2.17652	H	1.29923	−3.66726	0.96407
C	−1.66317	−4.20408	2.80226	H	−1.15420	2.11552	−2.66975
C	−2.28298	−5.28712	2.17667	H	−1.21206	4.32585	−3.78267
C	−2.87057	−5.11143	0.92220	H	−2.31307	6.25797	−2.66197
C	−2.84429	−3.86319	0.30120	H	−3.35232	5.94791	−0.42211
C	−0.99427	−0.73390	0.02342	H	−3.29586	3.73675	0.67957
C	−0.99471	0.73336	−0.02364	C	5.23405	−2.58936	−0.84489
C	0.22770	1.41242	0.22363	C	5.23247	2.59253	0.84484
C	0.23480	2.82368	0.71010	C	6.70429	−2.94293	−0.98745
C	−0.34160	3.11485	1.95834	H	4.70679	−2.70180	−1.80286
C	−0.29985	4.40498	2.48632	H	4.74088	−3.24414	−0.11227
C	0.31842	5.43453	1.77482	C	6.70249	2.94697	0.98748
C	0.89498	5.16117	0.53273	H	4.70510	2.70460	1.80279
C	0.85926	3.86901	0.00930	H	4.73894	3.24706	0.11223
C	1.48280	0.69398	0.16539	H	7.22069	2.83437	0.03010
C	2.72351	1.33304	0.39084	H	7.18687	2.29359	1.71975
C	3.93569	0.67771	0.21390	H	6.80823	3.98472	1.32191
C	3.93610	−0.67531	−0.21405	H	7.18831	−2.28931	−1.71975
C	2.72433	−1.33137	−0.39101	H	6.81067	−3.98064	−1.32181
C	1.48322	−0.69306	−0.16558	H	7.22238	−2.82995	−0.03005
C	0.22854	−1.41224	−0.22383				
C	0.23644	−2.82355	−0.71014				
C	−0.33951	−3.11514	−1.95850				
C	−0.29703	−4.40531	−2.48630				
C	0.32150	−5.43450	−1.77451				
C	0.89759	−5.16073	−0.53229				
C	0.86115	−3.86852	−0.00903				
C	−2.21882	1.39508	−0.32069				
C	−2.21998	2.76388	−0.91451				
C	−1.63277	2.95725	−2.17688				
C	−1.66654	4.20299	−2.80266				
C	−2.28661	5.28575	−2.17684				
C	−2.87354	5.10982	−0.92209				
C	−2.84636	3.86161	−0.30106				
H	−4.73035	2.31705	−0.85785				
H	−6.86235	1.15913	−0.46196				
H	−6.86158	−1.16325	0.46253				
H	−4.72881	−2.31987	0.85814				
H	−1.15193	−2.11634	2.66920				
H	−1.20818	−4.32675	3.78205				
H	−2.30874	−6.25938	2.66178				
H	−3.34916	−5.94974	0.42240				
H	−3.29429	−3.73851	−0.67921				
H	−0.81927	2.31498	2.51726				
H	−0.74772	4.60439	3.45668				
H	0.34992	6.44126	2.18320				
H	1.36966	5.95763	−0.03477				
H	1.29773	3.66807	−0.96369				