

Supporting Information

NIR-to-vis photon upconversion in rubrenes with increasing structural complexity

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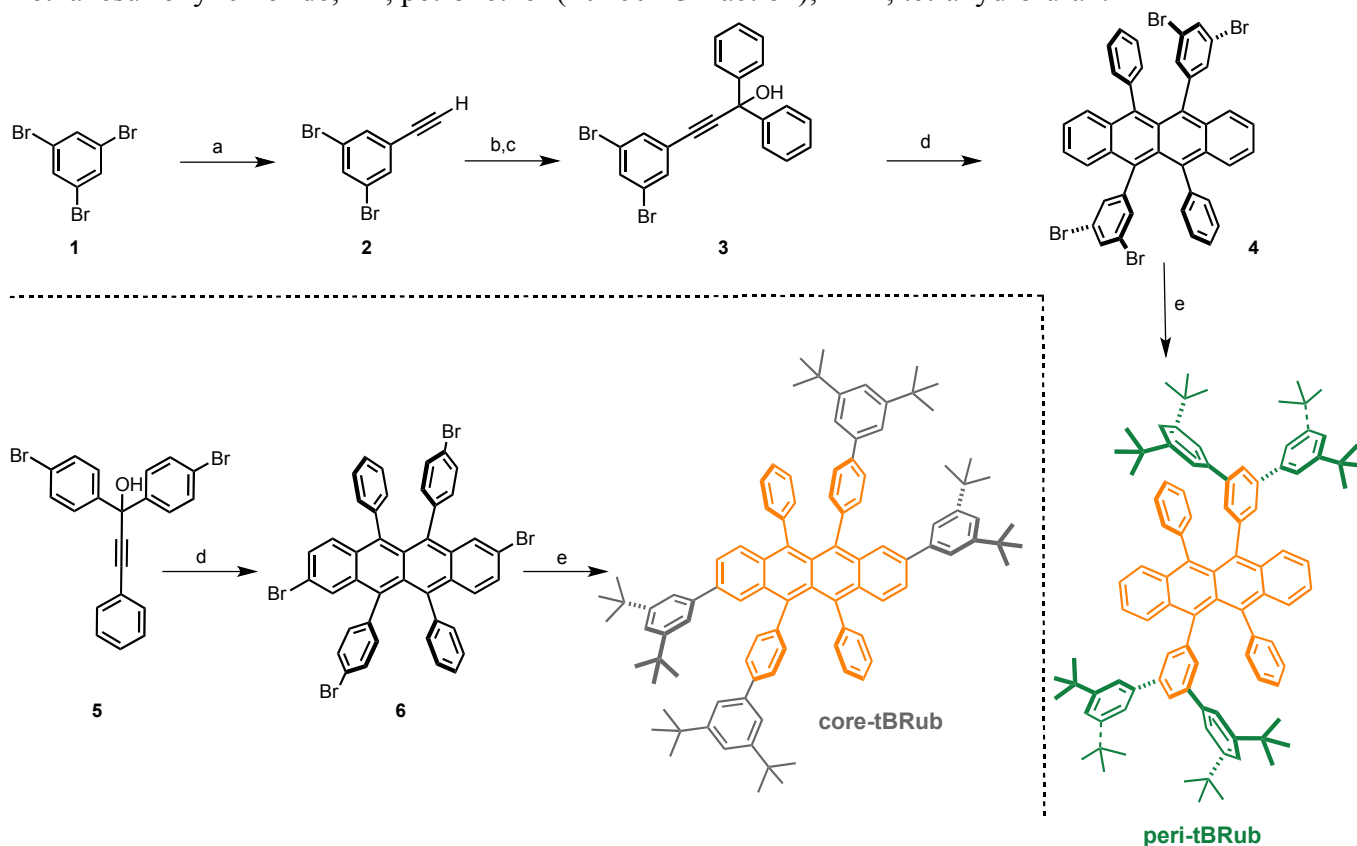
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General methods

All reagents and starting materials were obtained from commercial sources and used as received. Reaction solvents 1,2-dichloroethane and triethylamine were distilled from CaH₂, and THF was distilled from sodium/ benzophenone. All moisture-sensitive reactions were performed in oven-dried (230 °C) glassware under an atmosphere of dry argon. Thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV (254 nm), potassium permanganate (KMnO₄), ninhydrin, or vanillin. Column chromatography was performed using Merck silica 60 (40–63 μm particle size). ¹H and ¹³C NMR spectra were recorded on a NMR spectrometer at 400 MHz for ¹H and 101 MHz for ¹³C, respectively. ¹H and ¹³C NMR spectra are referenced to residual solvent (CDCl₃, 7.26 and 77.16 ppm for ¹H NMR and ¹³C NMR, respectively). Chemical shifts are reported in ppm, and multiplicities are indicated by s (singlet), d (doublet), t (triplet) and m (multiplet). Infrared spectra (IR) were recorded on a FTIR spectrometer equipped with a diamond ATR unit. Melting points were determined in open capillary tubes and are uncorrected.

Abbreviations: DCE, 1,2-dichloroethane; DCM, dichloromethane; Et₃N, triethylamine; EtOAc, ethyl acetate; EtOH, ethanol; Hep, heptane; LDA, lithium diisopropylamide; MeOH, methanol; MsCl, methanesulfonyl chloride; PE, petrol ether (40–60 °C fraction); THF, tetrahydrofuran.



Scheme S1. a) see ref. ¹; b) K₂CO₃, MeOH; b) LDA, THF; c) benzophenone; d) MsCl, Et₃N, DCE; e) (3,5-di-*tert*-butylphenyl)boronic acid, tetrakis(triphenylphosphine)palladium, K₂CO₃, toluene/EtOH/water.

Compound 2 (272 mg, 1.05 mmol, 1.0 equiv) is dissolved in dry THF (12 mL) under argon atmosphere. After cooling to -78 °C, LDA (0.44 mL, 2.5 M, 1.10 mmol, 1.05 equiv) was added and the mixture was stirred for 30 min. Then, the solution of benzophenone (191 mg, 1.05 mmol, 1.0 equiv) in dry THF (6.0 mL) was added dropwise, the cooling was removed and the mixture was stirred for 1 h at room temperature. The reaction mixture was quenched with 1.0 M HCl (20 mL), extracted with EtOAc and dried with Na₂SO₄. The crude obtained after filtration and evaporation was purified by column chromatography (15:1 Hep/EtOAc) to afford 3 (331 mg, 72%) as yellow oil.

TLC: $R_f = 0.59$ (1:10 EtOAc/PE);

^1H BMR (400 MHz, CDCl_3) δ 7.74 – 7.65 (m, 4H), 7.58 – 7.19 (m, 9H), 2.89 (s, 1H).

^{13}C BMR (101 MHz, CDCl_3) δ 144,81, 132,00, 129,93, 128,52, 128,02, 126,16, 124,52, 122,28, 93,14, 85,78, 74,95;

FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3408, 3059, 3027, 2224, 1649, 1539, 1489, 1448, 1102, 747, 696.

Compound **3** (252 mg, 0.57 mmol, 1.0 equiv) was dissolved in dry DCE (8.0 mL) under argon. The reaction mixture was cooled to 0 °C and Et_3N (0.2 mL, 1.42 mmol, 2.5 equiv) was added dropwise followed by MsCl (0.053 mL, 0.68 mmol, 1.2 equiv). After stirring for 24 h at room temperature, the mixture was further heated at 70 °C for 96 h. The volatiles were removed under vacuo and the crude obtained was purified by flash chromatography (gradient elution PE/DCM – 15:1 to 5:1) to afford **4** (89 mg, 37%) as orange solid.

TLC: $R_f = 0.47$ (10:1 PE/DCM);

m. p. >265 °C (decomp.);

^1H BMR (400 MHz, CDCl_3) δ 7.48 – 7.41 (m, 4H), 7.35 – 7.19 (m, 14H), 7.02 – 6.96 (m, 6H).

^{13}C BMR (101 MHz, CDCl_3) δ 144.96, 140.63, 137.66, 133.89, 133.70, 132.15, 131.76, 130.41, 130.14, 128.37, 127.35, 127.02, 126.77, 126.00, 125.75, 125.44, 122.06.

FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3060, 2923, 2852, 1954, 1765, 1577, 685.

Compound **4** (25 mg, 29 mmol, 1.0 equiv), (3,5-di-*tert*-butylphenyl)boronic acid (69 mg, 0.29 mmol, 10 equiv), K_2CO_3 (61 mg, 0.44 mmol, 15 equiv) and tetrakis(triphenylphosphine)palladium (6.8 mg, 5.9 mmol, 0.2 equiv) was dissolved in toluene/ethanol/water (10.5 mL, v/v-5:2:3.5) mixture. The mixture was heated at 95 °C for 27 h. After dilution with water, the reaction mixture was extracted with EtOAc, dried with Na_2SO_4 and filtered. The solvent was removed in vacuo and the crude obtained was purified by flash chromatography (gradient elution PE/DCM- 30:1 to 5:1) to afford **peri-tBRub** (22 mg, 58%) as an orange solid.

TLC: $R_f = 0.3$ (10:1 PE/DCM);

m.p. >265 °C (decomp.);

^1H BMR (400 MHz, CDCl_3) $\delta = 7.65 – 6.90$ (m, 36H), 1.54 – 1.31 (m, 72H);

^{13}C BMR (101 MHz, CDCl_3) δ 151.40, 151.01, 150.91, 142.13, 142.09, 141.62, 141.19, 137.21, 137.03, 136.57, 132.44, 130.77, 130.25, 130.08, 129.60, 126.84, 126.28, 125.06, 122.06, 121.65, 121.36, 35.05, 31.64;

FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3080, 2962, 2866, 1723, 1588, 1476, 1362, 866, 700.

Compound **5** (375 mg, 0.85 mmol, 1.0 equiv) was dissolved in dry DCE (10 mL) under argon. The reaction mixture was cooled to 0 °C and Et_3N (0.3 mL, 2.13 mmol, 2.5 equiv) was added dropwise followed by MsCl (0.08 mL, 1.02 mmol, 1.2 equiv). After stirring for 24 h at room temperature, the mixture was further heated at 70 °C for 98 h. The volatiles were removed under vacuo and the crude obtained was purified by flash chromatography (gradient elution PE/ CHCl_3 -10:1 to 6:1) to afford **6** (112 mg, 31%) as a red glass.

TLC: $R_f = 0.37$ (10:1 PE/DCM);

^1H NMR (400 MHz, CDCl_3) $\delta = 7.55$ (d, $J = 1.8$, 2H), 7.35 – 7.13 (m, 14H), 6.86 (d, $J = 6.8$, 2H), 6.71 (d, $J = 8.3$, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 140.68, 139.77, 136.64, 136.29, 133.41, 131.99, 131.29, 130.55, 129.45, 129.09, 128.82, 128.19, 127.65, 126.57, 120.73, 120.33.

FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3077, 2929, 1718, 1594, 1487, 1442, 1071, 972, 830, 700.

A mixture of **6** (34 mg, 40 mmol, 1.0 equiv), (3,5-di-*tert*-butylphenyl)boronic acid (94 mg, 0.4 mmol, 10 equiv.), K_2CO_3 (83 mg, 0.6 mmol, 15 equiv) and tetrakis(triphenylphosphine)palladium (9.3 mg, 8.0 mmol, 0.2 equiv) was dissolved in toluene/ethanol/water (6.0 mL, v/v-3:1:2). The mixture was heated at 95 °C for 27 h. After dilution with water, the mixture was extracted with DCM, dried with Na_2SO_4 and filtered. The solvent was removed in vacuo and the crude obtained was purified by flash chromatography (gradient elution PE/DCM- 20:1 to 5:1) to afford **core-tBRub** (52 mg, 50%) as a red glass.

TLC: $R_f = 0.15$ (10:1 PE/DCM);

^1H NMR (400 MHz, CDCl_3) $\delta = 7.75 – 7.64$ (m, 4H), 7.61 – 7.46 (m, 9H), 7.46 – 7.21 (m, 13H), 7.16 (t, $J = 7.5$, 4H), 7.07 (t, $J = 7.4$, 6H), 1.60 – 1.48 (m, 36H), 1.35 (s, 36H);

^{13}C NMR (101 MHz, CDCl_3) δ 151.15, 151.10, 151.08, 151.04, 151.02, 142.15, 141.28, 140.68, 140.57, 140.47, 139.81, 138.22, 137.55, 136.82, 132.48, 132.28, 130.73, 129.77, 129.68, 127.34, 127.24, 126.46, 125.62, 125.57, 124.67, 121.79, 121.76, 121.65, 121.47, 121.29, 35.11, 34.92, 31.69, 31.44.
FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3056, 2953, 1778, 1595, 1477, 1247, 874, 835, 700.

Table S1. First singlet and triplet energies of rubrene-based emitters along with their reorganization energies (λ) obtained from DFT calculations using B3LYP/6-31G(d) in vacuum.

	S_1 [eV]	λ_S [eV]	$S_1^*=S_1-\lambda_S$ [eV]	T_1 [eV]	λ_T [eV]	$T_1^*=T_1-\lambda_T$ [eV]	$2T_1^*-S_1^*$ [eV]
Rub	2.41	0.17	2.24	1.26	0.24	1.02	-0.20
tBRub	2.38	0.16	2.22	1.25	0.21	1.04	-0.15
peri-tBRub	2.39	0.17	2.22	1.25	0.24	1.02	-0.18
core-tBRub	2.28	0.16	2.11	1.22	0.22	1.00	-0.12

Geometry optimization was carried out using DFT as implemented in Orca software package². Equilibrium geometry of the ground state was obtained at the B3LYP functional level with the 6-31G(d) basis set in vacuum. Time-dependent DFT (TDDFT) was employed to calculate vertical excitation energies S_1 and T_1 . The reorganization energies for the singlet (λ_S) and triplet (λ_T) states were calculated through geometry optimization of S_1 and T_1 states.

λ_S and λ_T were found to be similar for all the rubrene emitters, i.e., ~ 0.17 eV and ~ 0.23 eV, respectively. Triplets exhibited larger reorganization energy than singlets. The calculations revealed that the reorganized triplet energies ($T_1 - \lambda_T$) of the **peri-tBRub** and **core-tBRub** are close or slightly lower as those of **Rub** and **tBRub** implying unmitigated potential for the triplet sensitization using **PdPc** sensitizer. Even though the reorganized singlet energies (S_1^*) fairly well corresponded to the FL maxima, the reorganized triplet energies (T_1^*) were significantly lower as compared to the literature values for rubrene ~ 1.14 eV.³ This indicated that the calculations overestimate the triplet reorganization energy erroneously implying that TTA is energetically unfavorable ($2T_1^* - S_1^* < 0$). Meanwhile, the experiments clearly evidenced TTA-UC in **Rub**, **tBRub** and **peri-tBRub**.

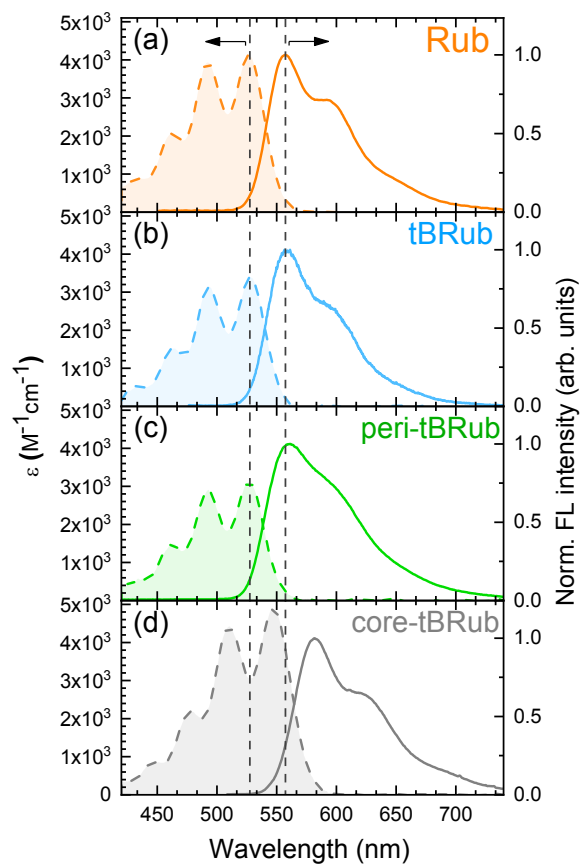


Fig. S1. Absorption (dashed lines) and fluorescence spectra (solid lines) of (a) **Rub**, (b) **tBRub**, (c) **peri-tBRub** and (d) **core-tBRub** in dilute toluene solution ($10^{-5}M$). Vertical dashed lines serve as guidelines for the eye.

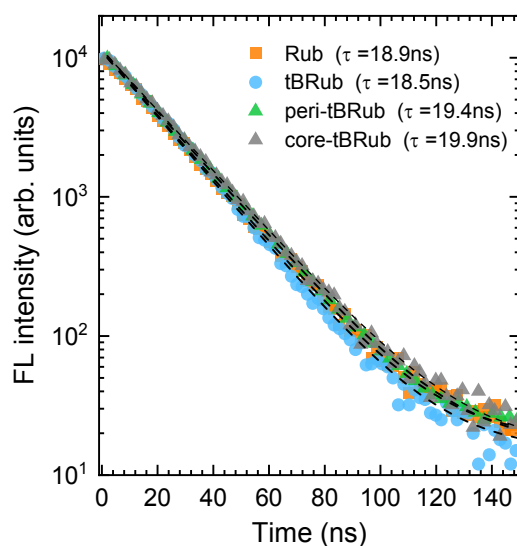


Fig. S2. Fluorescence transients of the investigated emitters doped in PS matrix at 0.01 wt% concentration. Dashed lines represent single-exponential fits with the decay time constants indicated.

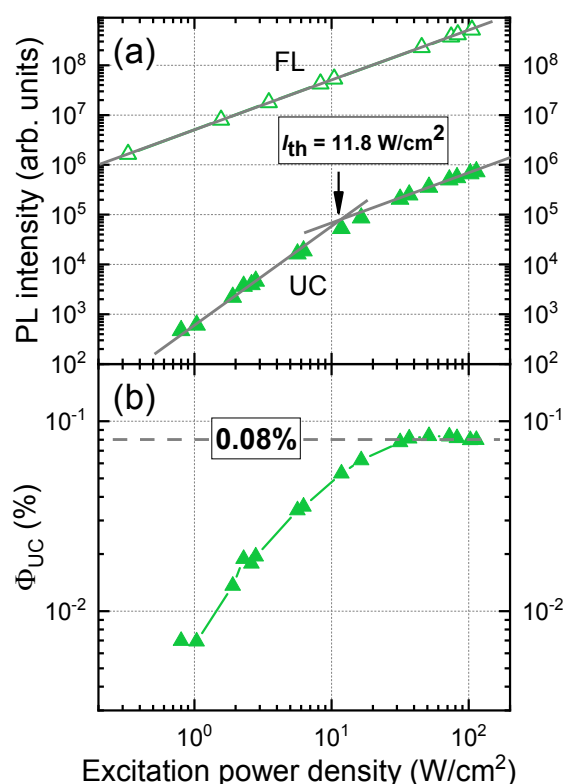


Fig. S3. (a) FL and UC intensities under CW excitation at 485 nm and 730 nm, respectively, as a function of excitation power density for **peri-tBRub** (18 mM):**PdPc** (15 μ M) in toluene solution. UC threshold (I_{th}) was determined from the intersection of quadratic and linear UC dependencies (indicated by an arrow). (b) UC quantum yield of the same system as a function of excitation power density.

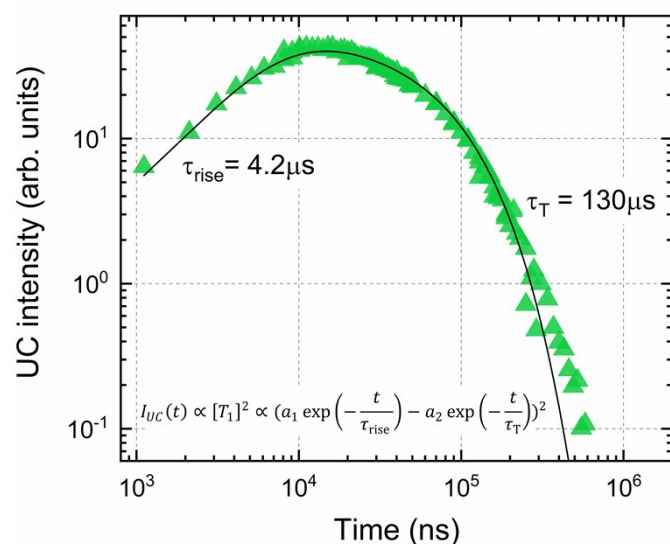


Fig. S4. UC transient (symbols) of the **peri-tBRub** (18 mM):**PdPc** (15 μ M) in toluene solution obtained using 730 nm pulsed excitation. Characteristic rise and triplet decay lifetimes, indicated. Line shows approximation of the experimental data with the formula, indicated.

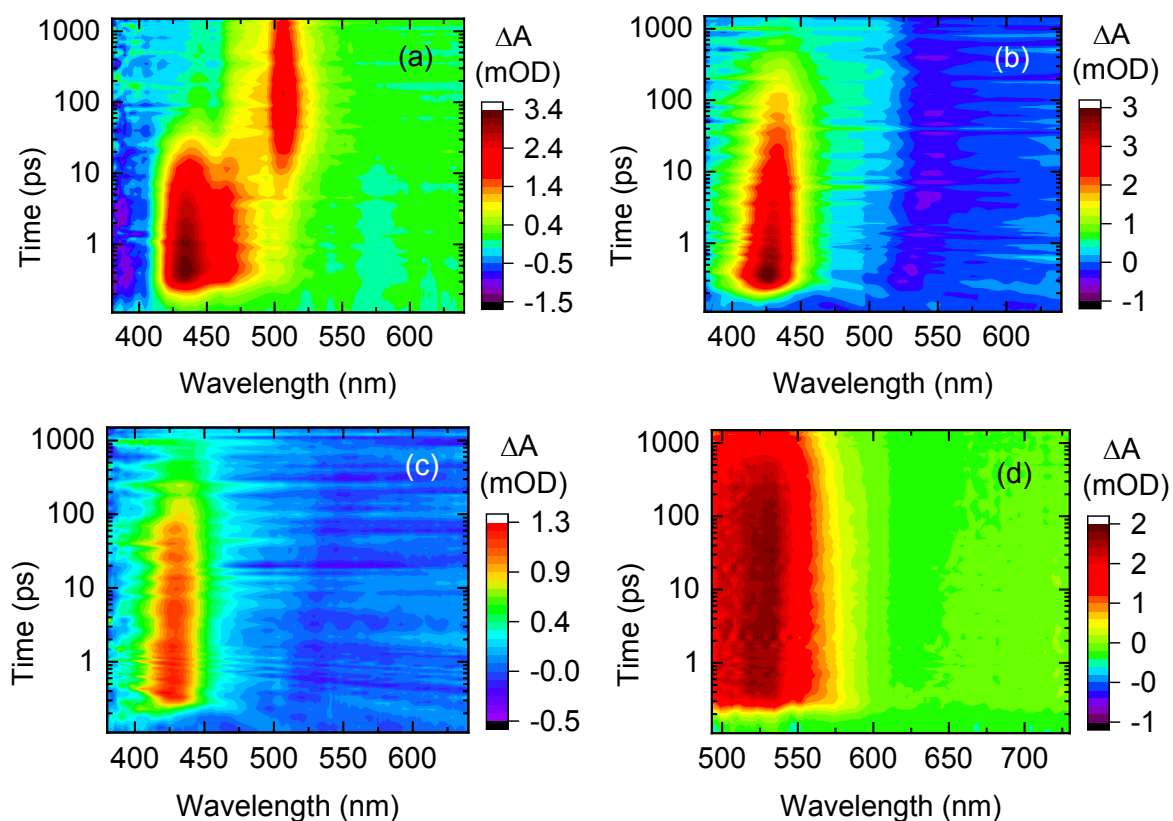


Fig. S5. Temporal-spectral maps of transient absorption signal for (a) **Rub**, (b) **tBRub**, (c) **peri-tBRub** and (d) **core-tBRub** neat films excited with 485 nm laser pulses.

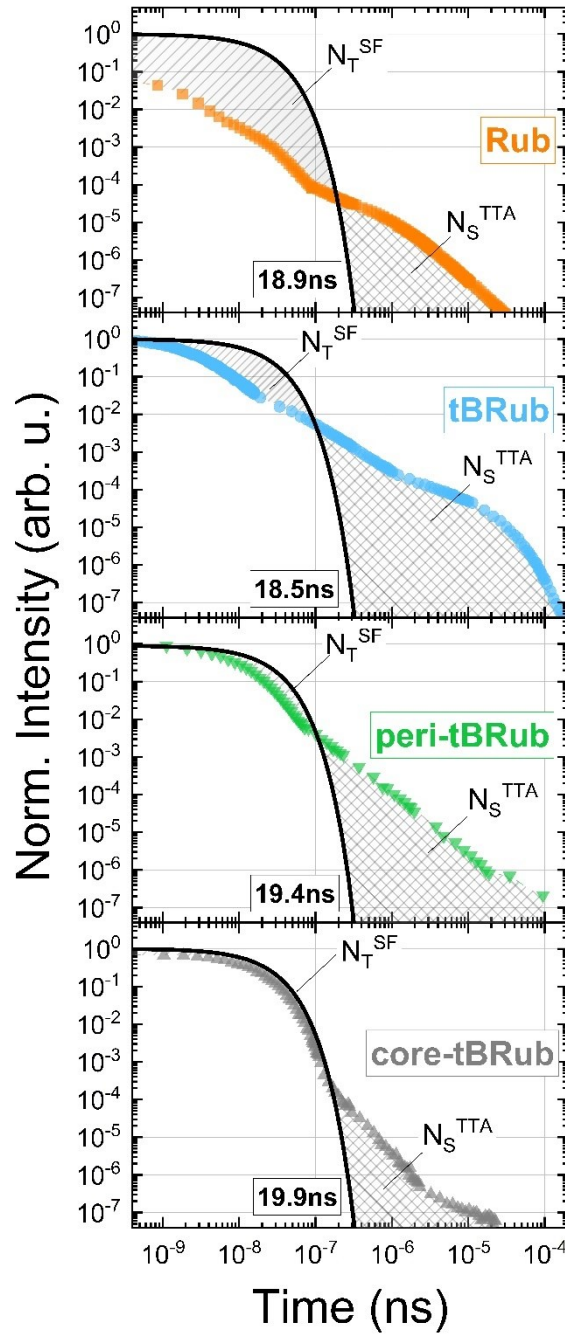


Fig. S6. FL transients of each rubrene film scaled so that their integrals correspond to their Φ_{FL} (see Figure 3). Prompt-only reference transients are shown by solid line. The integrals representing N_T^{SF} and N_S^{TTA} for each rubrene film, indicated.

Table S2. The main parameters necessary for the evaluation of TTA efficiency in the neat films of different rubrene emitters

Rubrene emitter	N_T^{SF}	N_S^{TTA}	Φ_{FL}^{prompt} (%)	TTA eff. (%)
Rub	18.8	0.03	1.0	18.5
tBRub	14.2	2.5	22.4	77.3
peri-tBRub	7.4	0.7	59.5	15.4
core-tBRub	7.0	0.02	62.0	0.6

N_T^{SF} – area indicated in Fig. S6 representing the number of triplets created via SF

N_S^{TTA} – area indicated in Fig. S6 representing the number of singlets created via TTA

Φ_{FL}^{prompt} – prompt FL quantum yield obtained from the corresponding integral in the FL transient

TTA eff. – TTA efficiency calculated according to the Eq. 1.

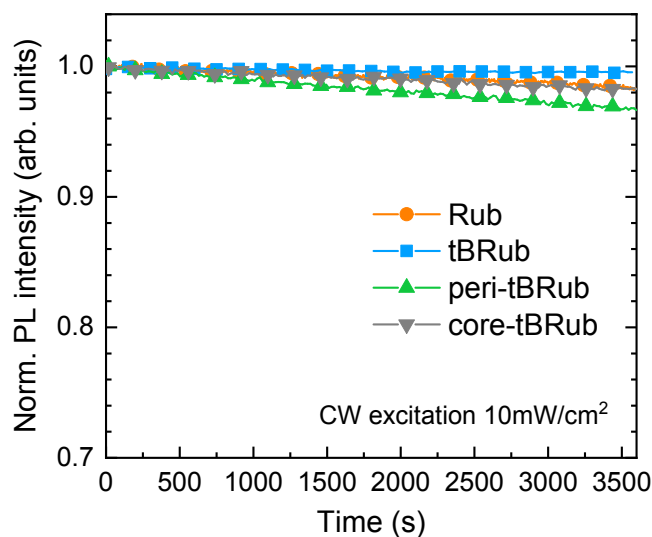


Fig. S7. Photostability data of the studied rubrene neat films (indicated) over the period of 1 hour.

Photostability measurements of the encapsulated rubrene films show insignificant PL signal degradation (less than 2%) at least over the period of 1 hour. The degradation was found to depend mostly on the quality of encapsulation rather on the rubrene emitter itself.

REFERENCES

- 1 E. C. Constable, C. E. Housecroft, M. Neuburger, S. Reymann and S. Schaffner, *Eur. J. Org. Chem*, 2008, **2008**, 1597–1607.
- 2 F. Neese, *WIREs Comput. Mol. Sci.*, 2012, **2**, 73–78.
- 3 T. N. Singh-Rachford and F. N. Castellano, *J. Phys. Chem. A*, 2008, **112**, 3550–3556.