

SUPPLEMENTARY INFORMATION

Understanding the limitations of NIR-to-visible photon upconversion in metallophthalocyanine- sensitized rubrene systems

Edvinas Radiunas,¹ Steponas Raišys,¹ Saulius Juršėnas,¹ Augustina Jozeliūnaitė,² Tomas Javorskis,² Ugnė Šinkevičiūtė,² Edvinas Orentas², Karolis Kazlauskas^{1}*

¹Institute of Photonics and Nanotechnology, Vilnius University, Saulėtekio av. 3, LT-10257 Vilnius, Lithuania

²Department of Organic Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania

E-mail: Karolis.kazlauskas@ff.vu.lt

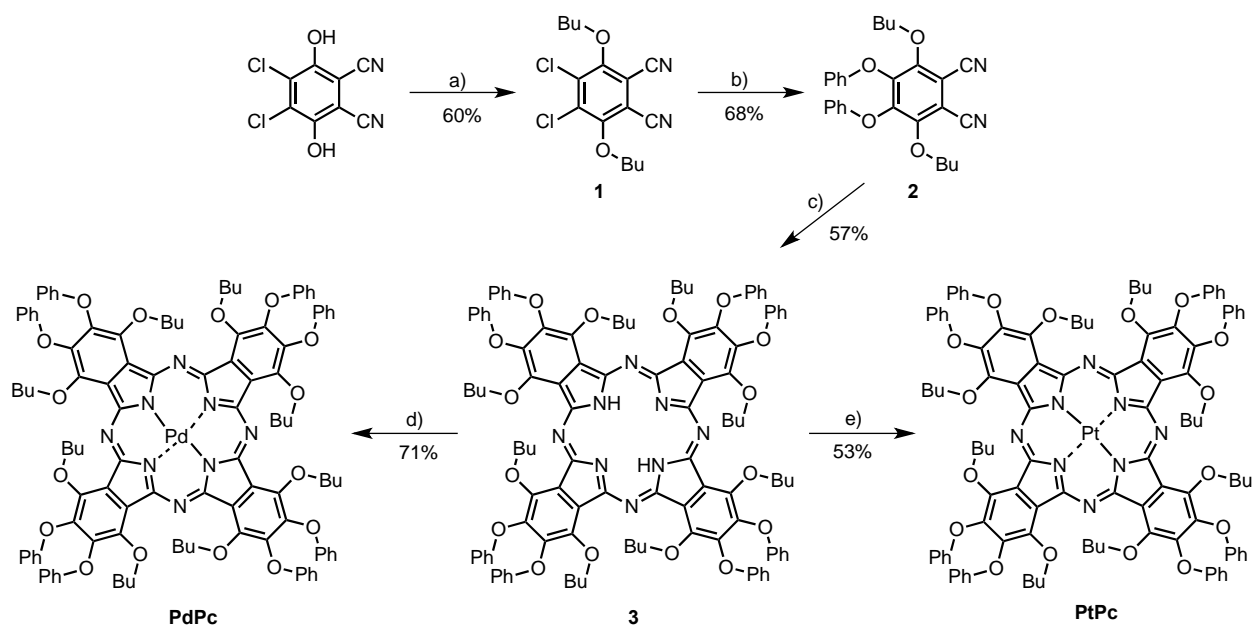
SYNTHESIS AND IDENTIFICATION

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 CaH_2 , and THF was distilled from sodium/ benzophenone. Brine refers to a saturated solution of sodium chloride. All moisture-sensitive reactions were performed in oven-dried ($230\text{ }^\circ\text{C}$) 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 (KMnO_4), ninhydrin, or vanillin. Column chromatography was performed using Merck silica 60 (40–63 μm particle size). ^1H and ^{13}C NMR spectra were recorded on a NMR spectrometer at 400 MHz for ^1H and 101 MHz for ^{13}C , respectively. ^1H and ^{13}C NMR spectra are referenced to residual solvent (CDCl_3 , 7.26 and 77.16 ppm for ^1H NMR and ^{13}C NMR, respectively). When necessary, assignments were obtained by reference to COSY, HSQC, and HMBC correlations. Chemical shifts are reported in ppm, and multiplicities are indicated by br (broad), s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sxt (sextet), sept (septet), m (multiplet), and combinations thereof. 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. HRMS was recorded on Bruker Daltonics microTOF-II spectrometer equipped with ESI ion source in positive mode.

Abbreviations: DCE, 1,2-dichloroethane; DCM, dichloromethane; DMF, dimethylformamide; DMSO, dimethylsulfoxide; EtOAc, ethyl acetate; Hex, hexane; MeOH, methanol; MsCl, methanesulfonyl chloride; PE, petrol ether (40–60 $^\circ\text{C}$ fraction).

Phthalocyanines: **PdPc** and **PtPc**



a) *n*-BuBr, K₂CO₃, KI, DMF, 80°C; b) phenol, K₂CO₃, DMSO, 90°C; c) *n*-butanol, Li, 135°C; d) Pd(OAc)₂, *n*-butanol, 135 °C; e) PtCl₂, benzonitrile, 191°C.

3,6-dibutoxy-4,5-dichlorophthalonitrile (1)

A mixture of 2,3-dichloro-5,6-dicyanohydroquinone (1.0 g, 4.37 mmol, 1.0 equiv), *n*-BuBr (1.4 mL, 13.10 mmol, 3.0 equiv), K₂CO₃ (3.62 g, 26.22 mmol, 6.0 equiv) and KI (1.45 g, 8.74 mmol, 2.0 equiv) in DMF (20 mL) was heated at 80 °C for 3 hours. The reaction mixture was cooled down to r.t., diluted with 1.0 M HCl solution and extracted with ethyl acetate. The organic phase was washed with water and brine, dried over anhydrous Na₂SO₄ and evaporated to dryness. The crude was purified by flash chromatography (PE:CHCl₃ 1:1, R_f = 0.31) to afford 899 mg (60 %) of **1** as a yellowish solid.

Spectral data were in accordance with a literature. [1]

3,6-dibutoxy-4,5-diphenoxyphthalonitrile (2)

A mixture of **1** (0.72 g, 2.11 mmol, 1.0 equiv), phenol (0.99 g, 10.58 mmol, 5.0 equiv) and K₂CO₃ (1.46 g, 10.58 mmol, 5.0 equiv) in dry DMSO (20 mL) was heated at 90 °C for 1.5 hours under argon. The reaction mixture was cooled down to r.t., diluted with 1.0 M HCl solution and extracted with DCM. The organic phase was washed with water and brine, dried over anhydrous Na₂SO₄ and evaporated to dryness. The crude was purified by flash chromatography (PE:DCM 1:2, R_f = 0.4) to afford 659 mg (68 %) of **2** as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.23 (t, *J* = 7.8 Hz, 4H, ArH), 7.05 (t, *J* = 7.2 Hz, 2H, ArH), 6.67 (d, *J* = 8.6 Hz, 4H, ArH), 4.12 (t, *J* = 6.4 Hz, 4H, OCH₂), 1.64 – 1.56 (m, 4H, CH₂), 1.39 – 1.28 (m, 4H, CH₂), 0.84 (t, *J* = 7.4 Hz, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃): δ = 156.45, 152.94, 146.57, 129.70, 123.64, 115.56, 112.86, 106.48, 75.78, 31.97, 18.87, 13.77.

Metal-free phthalocyanine (3)

A solution of **2** (436 mg, 0.96 mmol, 1.0 equiv) dissolved in dry *n*-butanol (15 ml) was refluxed at 135 °C for 30 min under argon. Then, Li metal (133 mg, 19.14 mmol, 20.0 equiv) was added and reflux was continued for a further 3 hours. After cooling down the reaction mixture to r.t., excess of glacial AcOH was added and continued to stir at rt for 30 min. Then solvent was removed, crude dissolved in DCM and washed with H₂O and brine, dried over anhydrous Na₂SO₄ and evaporated to dryness. The crude was purified by flash chromatography (PE:CHCl₃ 1:1 to 1:2, R_f = 0.42 (1:1)) to afford 247 mg (57%) of **3** as a green solid; mp 305 – 308 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.25 (dd, *J* = 8.3, 7.6 Hz, 16H, ArH), 7.07 (d, *J* = 7.9 Hz, 16H, ArH), 7.00 (t, *J* = 7.3 Hz, 8H, ArH), 4.83 (t, *J* = 6.8 Hz, 16H, OCH₂), 1.82 – 1.70 (m, 16H, CH₂), 1.33 – 1.21 (m, 16H, CH₂), 0.72 (t, *J* = 7.4 Hz, 24H, CH₃).

¹³C NMR (100 MHz, CDCl₃): δ = 158.71, 147.29, 144.64, 129.29, 122.18, 115.88, 76.53, 32.25, 19.15, 14.08.

FT-IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$ 3294 (N-H), 2957, 2930, 2870 (C-H), 1720, 1591 (C=N), 1488, 1453, 1406 (C-H), 1270 (=C-N), 1201 (C-O), 1163, 1079, 1070, 1020, 973, 932, 814, 746, 658 cm^{-1} .

HRMS (ESI) calc. for $\text{C}_{112}\text{H}_{114}\text{N}_8\text{O}_{16}$ (M+H): 1828.8458; Found: 1828.8459.

Palladium (II) phthalocyanine (PdPc)

A mixture of **3** (20mg, 0.011 mmol, 1.0 equiv) and $\text{Pd}(\text{OAc})_2$ (18 mg, 0.066 mmol, 6.0 equiv) in dry *n*-butanol (2 mL) was refluxed at 135 °C for 24 hours under argon. After cooling down to rt, the solvent was removed. The crude was purified by flash chromatography (PE: CHCl_3 2:1, R_f = 0.48), then dissolved in minimum amount CHCl_3 , precipitated with MeOH, filtered and washed with MeOH to afford 15 mg (71%) of **4** as a green solid; mp >330 °C.

^1H NMR (400 MHz, CDCl_3): δ = 7.26 (t, J = 8.0 Hz, 16H, ArH), 7.08 (d, J = 7.9 Hz, 16H, ArH), 7.01 (t, J = 7.3 Hz, 8H, ArH), 4.87 (t, J = 6.9 Hz, 16 H, OCH_2), 1.84 – 1.72 (m, 16H, CH_2), 1.34 – 1.21 (m, 16H, CH_2), 0.73 (t, J = 7.4 Hz, 24H, CH_3).

^{13}C NMR (100 MHz, CDCl_3): δ = 158.72, 147.19, 144.45, 142.02, 129.28, 126.73, 122.15, 115.85, 76.65, 32.22, 19.14, 14.09.

FT-IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$ 2956, 2931, 2870 (C-H), 1722, 1591 (C=N), 1488, 1451, 1405 (C-H), 1282 (=C-N), 1201 (C-O), 1137, 1068, 965, 938, 746, 685 cm^{-1} .

HRMS (ESI) calc. for $\text{C}_{112}\text{H}_{112}\text{N}_8\text{O}_{16}\text{Pd}$ (M+H): 1931.7335; Found: 1931.7309.

Platinum (II) phthalocyanine (PtPc)

A mixture of **3** (20 mg, 0.011 mmol, 1.0 equiv) and PtCl_2 (3.5 mg, 0.013 mmol, 1.2 equiv) in dry benzonitrile (3 mL) was heated at reflux for 2 hours, and then the solvent was partially distilled off, precipitated with MeOH, filtered and washed with MeOH. The crude was purified by flash chromatography (PE: CHCl_3 3:1 R_f = 0.2) to afford 12 mg (53%) of **5** as a green solid; mp 274 – 276 °C.

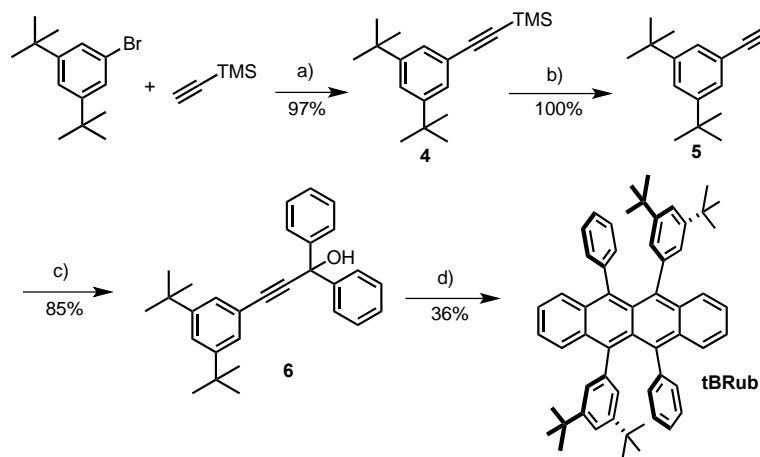
^1H NMR (400 MHz, CDCl_3): δ = 7.26 (t, J = 8.0 Hz, 16H, ArH), 7.08 (d, J = 7.8 Hz, 16H, ArH), 7.01 (t, J = 7.3 Hz, 8H, ArH), 4.86 (t, J = 6.9 Hz, 16H, OCH_2), 1.83 – 1.73 (m, 16H, CH_2), 1.33 – 1.21 (m, 16H, CH_2), 0.73 (t, J = 7.4 Hz, 24H, CH_3).

^{13}C NMR (100 MHz, CDCl_3): δ = 158.70, 147.53, 144.57, 140.46, 129.29, 126.33, 122.16, 115.84, 76.66, 32.20, 19.15, 14.09.

FT-IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$ 2956, 2922, 2870 (C-H), 1721, 1591 (C=N), 1488, 1452, 1406 (C-H), 1283 (=C-N), 1202 (C-O), 1142, 1069, 970, 938, 747, 684 cm^{-1} .

HRMS (ESI) calc. for $\text{C}_{112}\text{H}_{112}\text{N}_8\text{O}_{16}\text{Pt}$ (M+H): 2021.7944; Found: 2021.7990.

t-butyl-substituted rubrene: **tBRub**



a) Pd(PPh₃)₄, CuI, Ph₃P, TEA, 90°C; b) DCM, MeOH, K₂CO₃, rt; c) *n*-BuLi, THF, -78°C to rt; d) MsCl, TEA, DCE rt to 130 °C.

((3,5-di-*tert*-butylphenyl)ethynyl)trimethylsilane (4)

A mixture of 1-bromo-3,5-di-*tert*-butylbenzene (1.30 g, 4.83 mmol, 1.0 equiv), Pd(PPh₃)₄ (279 mg, 0.24 mmol, 0.05 equiv.), CuI (46 mg, 0.24 mmol, 0.05 equiv.) and PPh₃ (76 mg, 0.29 mmol, 0.06 equiv.) was dissolved in triethylamine (35 ml) under argon. TMS-acetylene was added and the reaction mixture was heated at 90 °C for 16 hr. After cooling to rt, the mixture was filtered through CELITE and evaporated to dryness. The crude was purified by flash chromatography (PE) to afford 1.34 g (97%) of **4** as a colorless solid.

Spectral data were in accordance with a literature.[2]

1,3-di-*tert*-butyl-5-ethynylbenzene (5)

To a solution of K₂CO₃ (0.97 g, 7.0 mmol, 1.5 equiv.) in MeOH/DCM (24 mL/5.3 mL) mixture compound **4** (1.34 g, 4.67 mmol, 1.0 equiv.) was added under argon. The reaction mixture was stirred for 1 h at rt, then diluted with DCM and filtered. The organic phase was washed with sat. NH₄Cl solution and water, dried with Na₂SO₄, filtered and evaporated to dryness to afford 1.00 g (100%) of **5**.

Spectral data were in accordance with a literature.[2]

3-(3,5-di-*tert*-butylphenyl)-1,1-diphenylprop-2-yn-1-ol (**6**)

Compound **5** (1.00 g, 4.67 mmol, 1.0 equiv.) was dissolved in dry THF (25 mL) under argon. The solution was cooled to -78 °C and *n*-BuLi (1.96 mL (2.5 M), 4.90 mmol, 1.05 equiv.) was added dropwise. After 30 min, a solution of benzophenone (0.85 g, 4.67 mmol, 1.0 equiv.) in dry THF (4.0 mL) was added and the reaction mixture was allowed to reach room temperature. After stirring overnight, the mixture was diluted with 1.0 M HCl and extracted with ethylacetate. The combined organic phase was dried with Na₂SO₄, filtered and evaporated to dryness. The crude was purified by flash chromatography (20:1 PE/EtOAc, *R*_f = 0,37) to afford 1.569 g (85%) of **6** as colorless solid; mp 99 – 100 °C. Compound **6** was immediately used for the next step.

¹H NMR (400 MHz, CDCl₃): δ 7,74–7,68 (m, 4H), 7.42 (t, *J* = 1,9 Hz, 1H), 7,40–7,33 (m, 6H), 7,32–7,28 (m, 2H), 2,89 (s, 1H), 1,33 (s, 18H);

¹³C BMR (101 MHz, CDCl₃) δ 150,72, 144,99, 128,13, 127,93, 127,50, 125,95, 125,84, 122,98, 121,21, 90,16, 88,14, 74,73, 34,66, 31,16;

FT-IR (neat) $\nu_{\max}/\text{cm}^{-1}$ 3543, 3070, 2964, 2869, 2224, 1589, 1489, 1449, 1329, 1163, 1058, 997, 920, 880, 770, 699.

tBRub

Compound **6** (250 mg, 0.63 mmol, 1.0 equiv.) was dissolved in dry DCE (5.0 mL) under argon. The mixture was cooled to 0 °C and then, TEA (0.22 mL, 1.58 mmol, 2.5 equiv.) was added followed by MsCl (0.059 mL, 0.76 mmol, 1.2 equiv.). After stirring at rt for 24 hr, the reaction mixture was heated at 130 °C for 7 hr. The volatiles were removed in vacuo and the crude was purified by flash chromatography (PE → 100:1 PE/DCM → 60:1 PE/DCM → 40:1 PE/DCM → 25:1 PE/DCM) and then crystallized from MeOH to afford 87 mg (36%) of **tBRub** as orange crystals; mp >265 °C (decomp.)

¹H NMR (400 MHz, CDCl₃): δ 7,23–6,63 (m, 24H), 1,28 (s, 36H).

¹³C NMR (100 MHz, CDCl₃): δ 148.75, 141.90, 140.81, 138.71, 137.22, 132.65, 130.72, 130.61, 129.04, 127.07, 126.99, 126.95, 126.87, 126.20, 124.76, 124.70, 120.70, 34.86, 31.66.

FT-IR $\nu_{\max}/\text{cm}^{-1}$ 3053, 2963, 2867, 1592, 1443, 1392, 1248, 872, 691.

MS (MALDI-TOF) calc. for C₅₈H₆₀ (M⁺): 757.12; Found: 757.96.

COPIES OF NMR SPECTRA

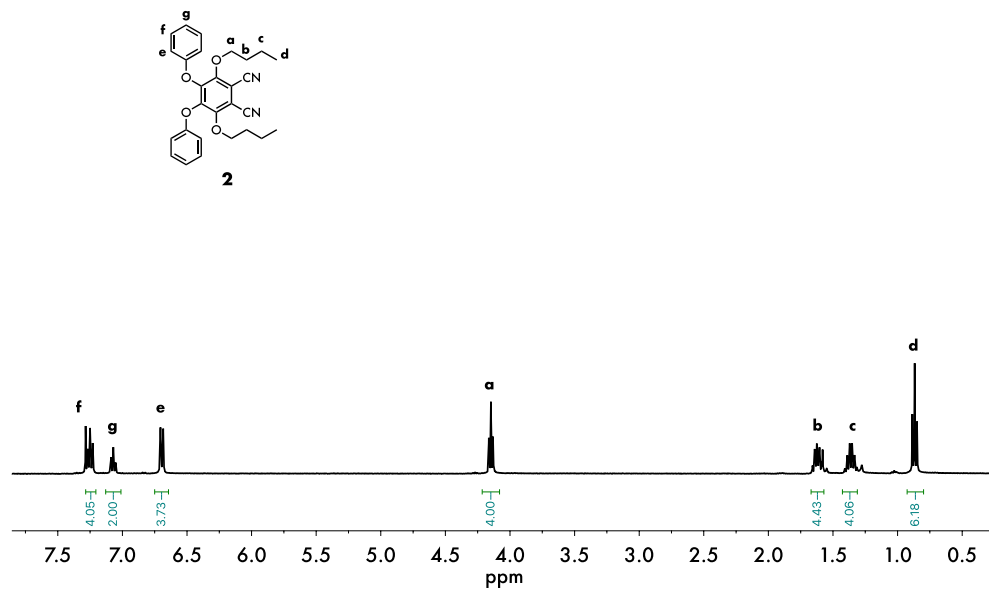


Fig. S1. ^1H NMR spectrum of **2** (400 MHz, CDCl_3).

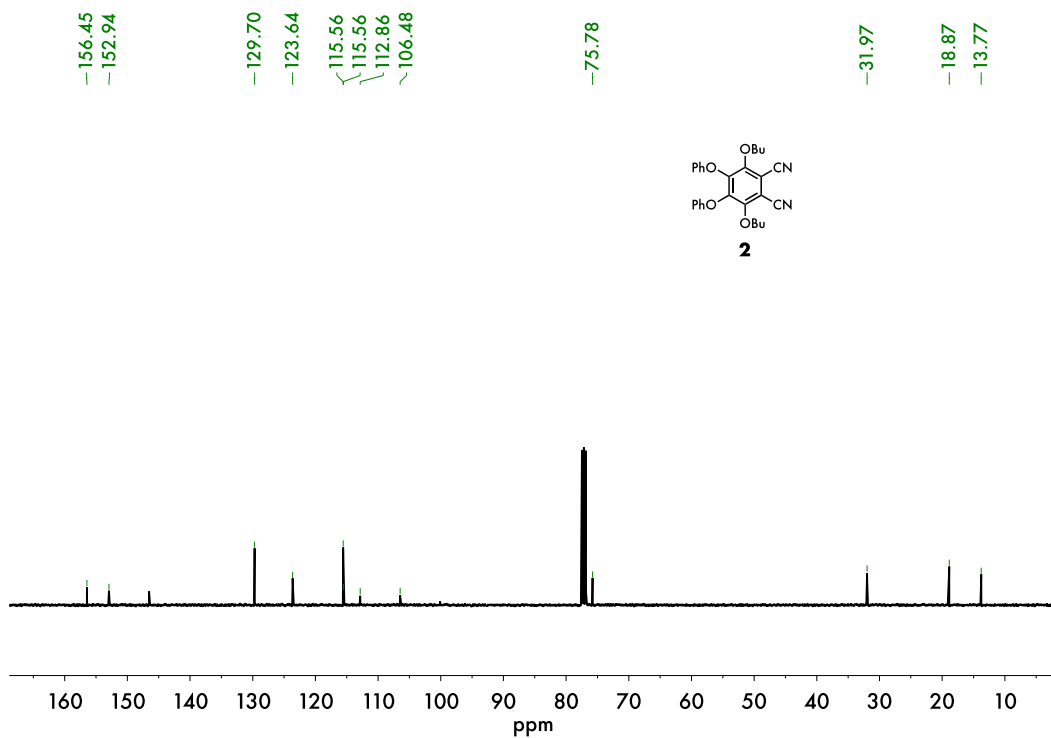


Fig. S2. ^{13}C NMR spectrum of **2** (101 MHz, CDCl_3).

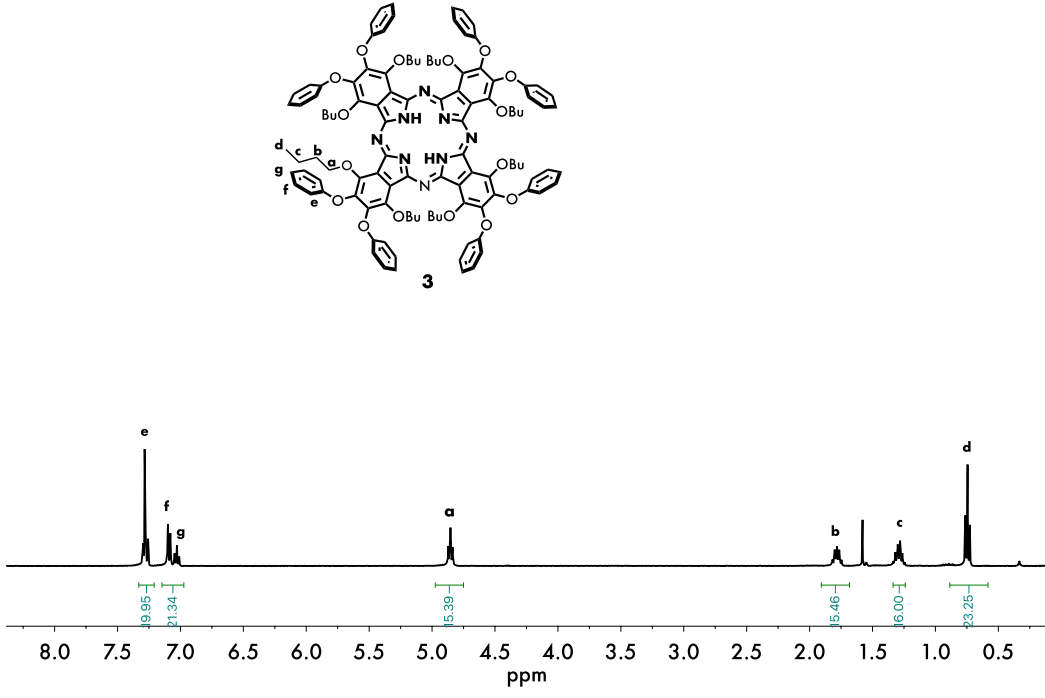


Fig. S3. ^1H NMR spectrum of **3** (400 MHz, CDCl_3).

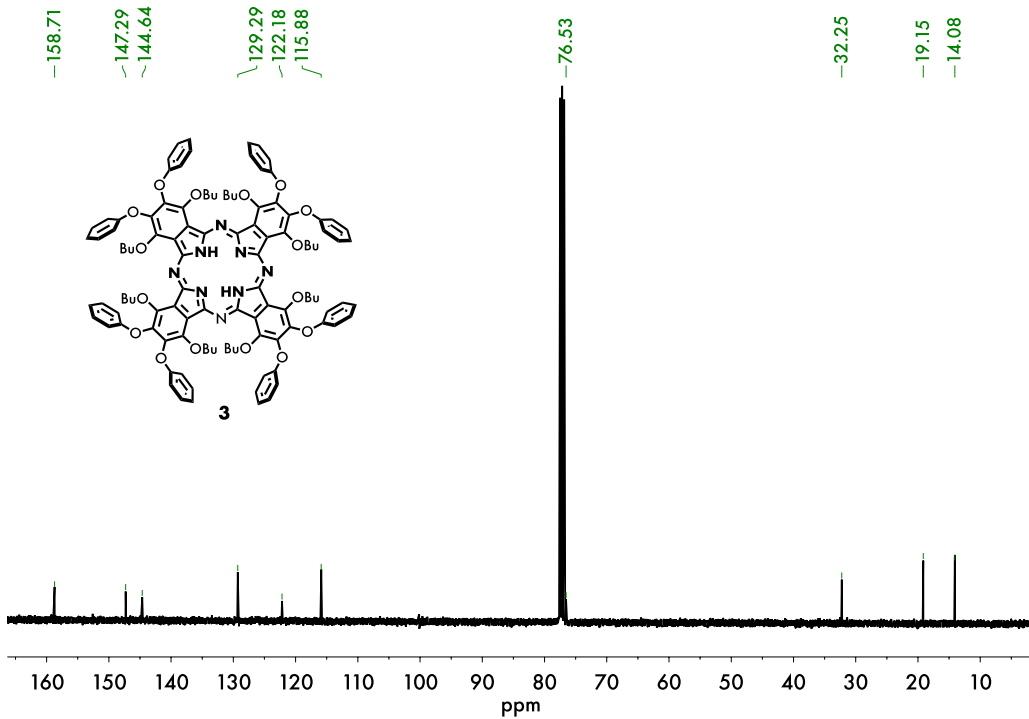


Fig. S4. ^{13}C NMR spectrum of **3** (101 MHz, CDCl_3).

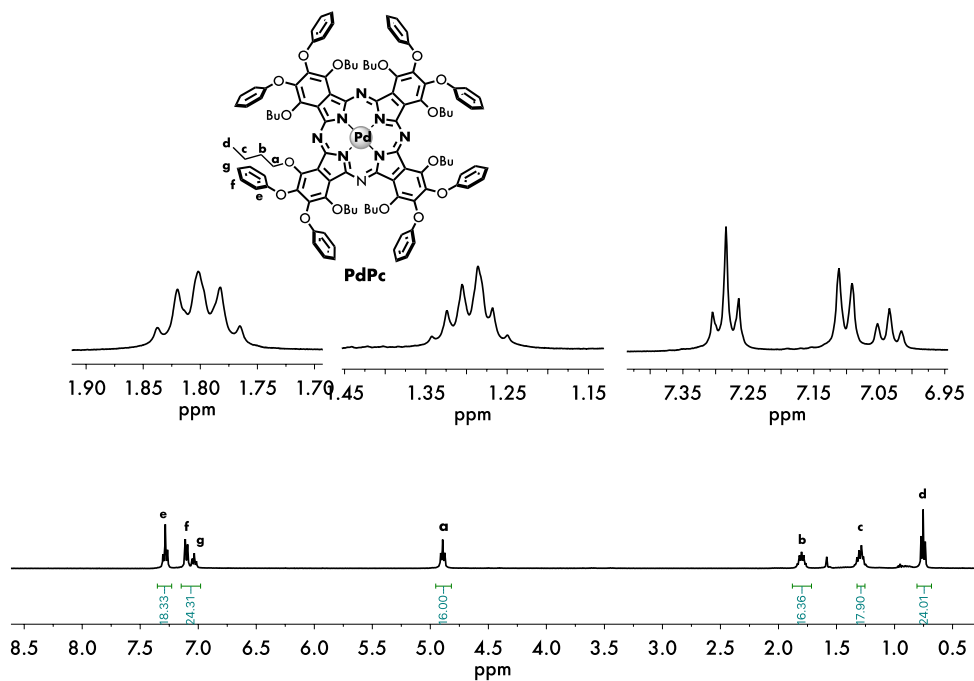


Fig. S5. ^1H NMR spectrum of PdPc (400 MHz, CDCl_3).

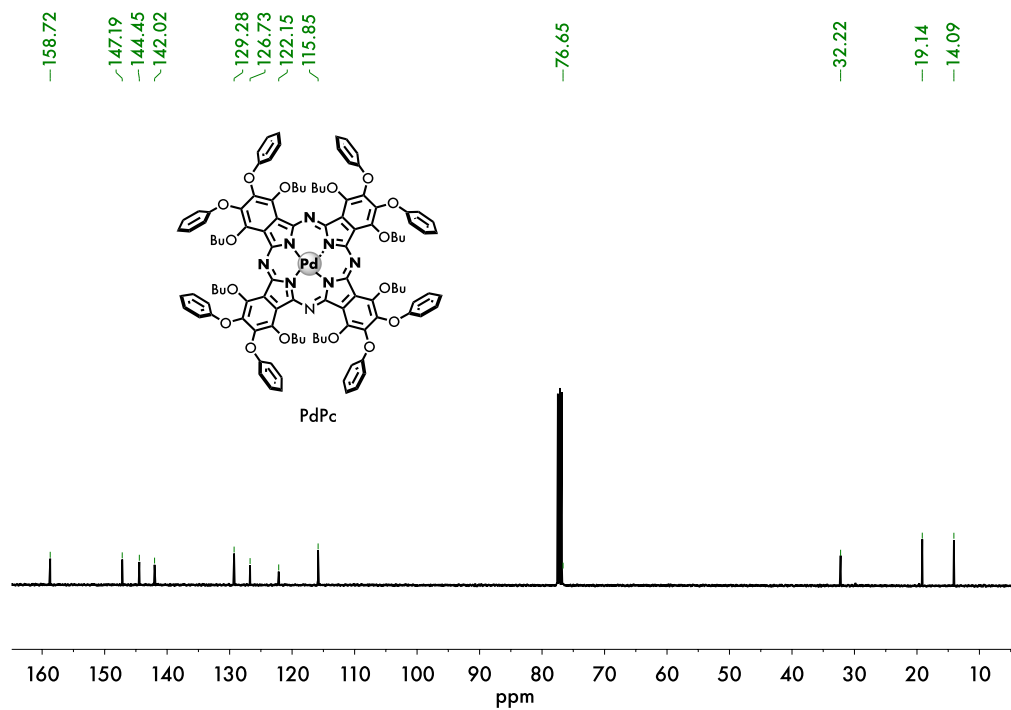


Fig. S6. ^{13}C NMR spectrum of PdPc (101 MHz, CDCl_3).

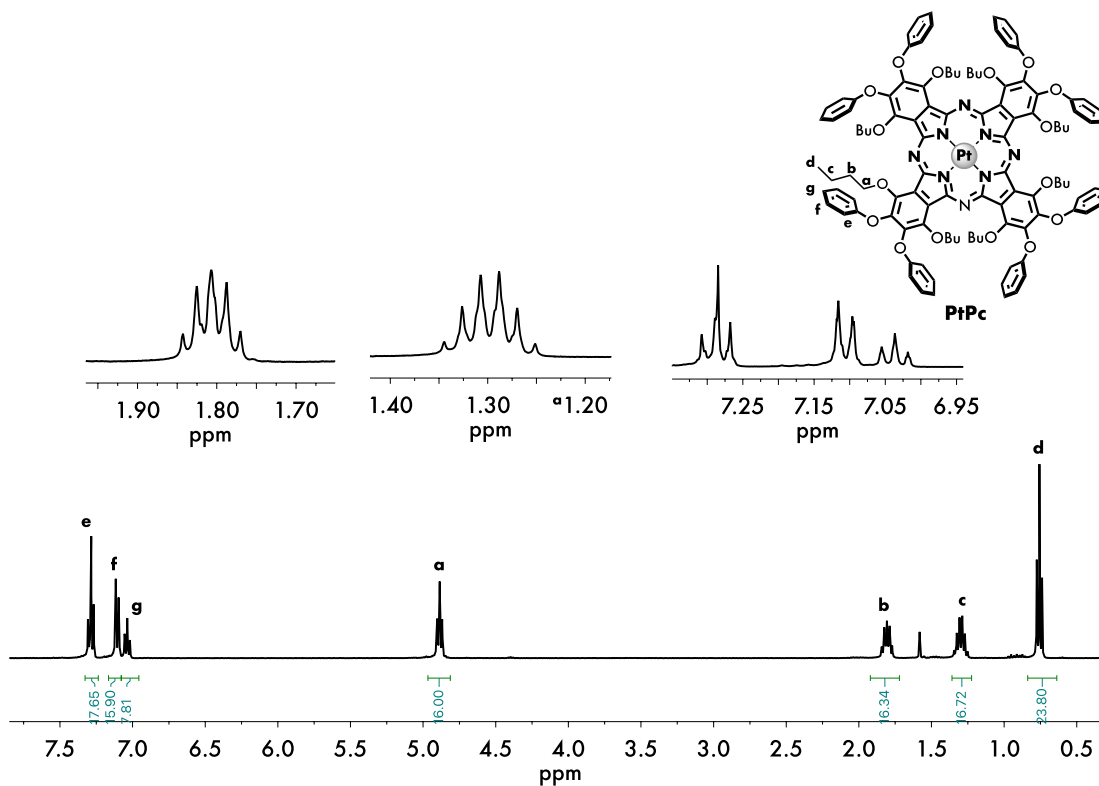


Fig. S7. ^1H NMR spectrum of PtPc (400 MHz, CDCl_3).

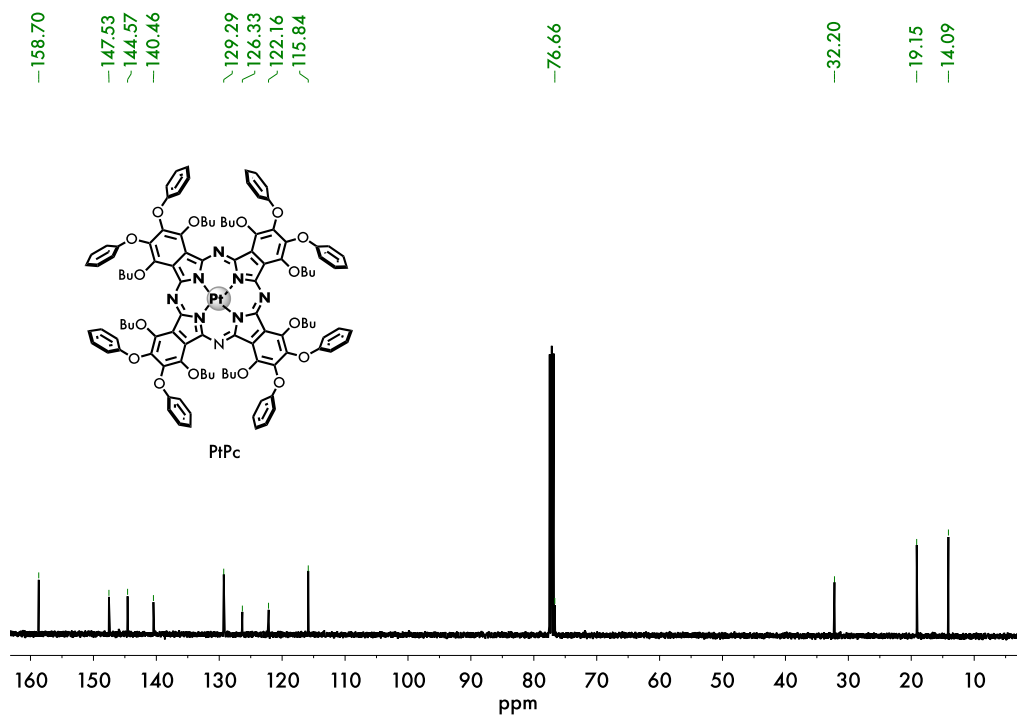


Fig. S8. ^{13}C NMR spectrum of PtPc (101 MHz, CDCl_3).

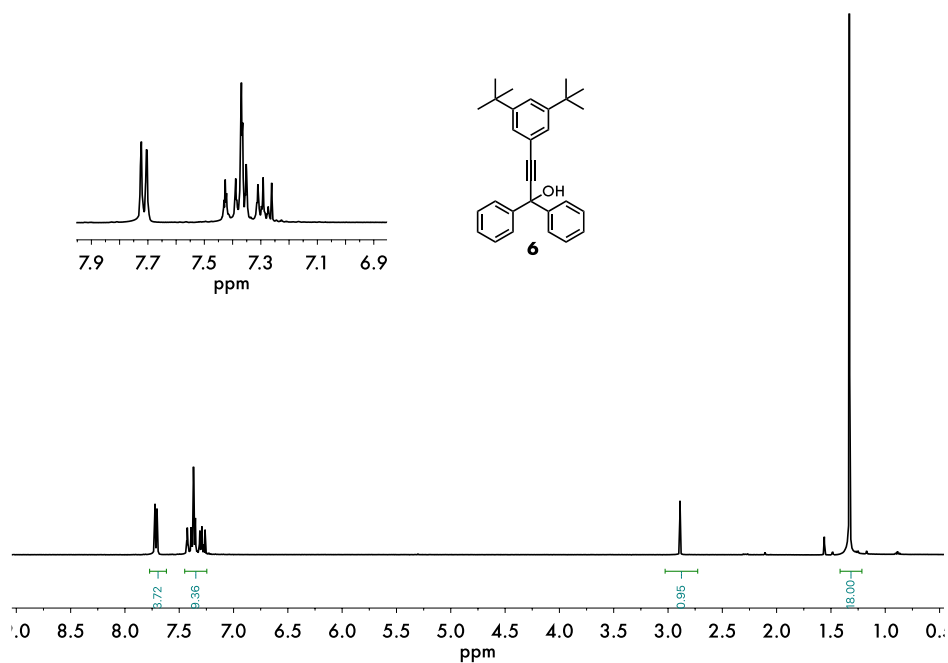


Fig. S9. ¹H NMR spectrum of **6** (400 MHz, CDCl₃).

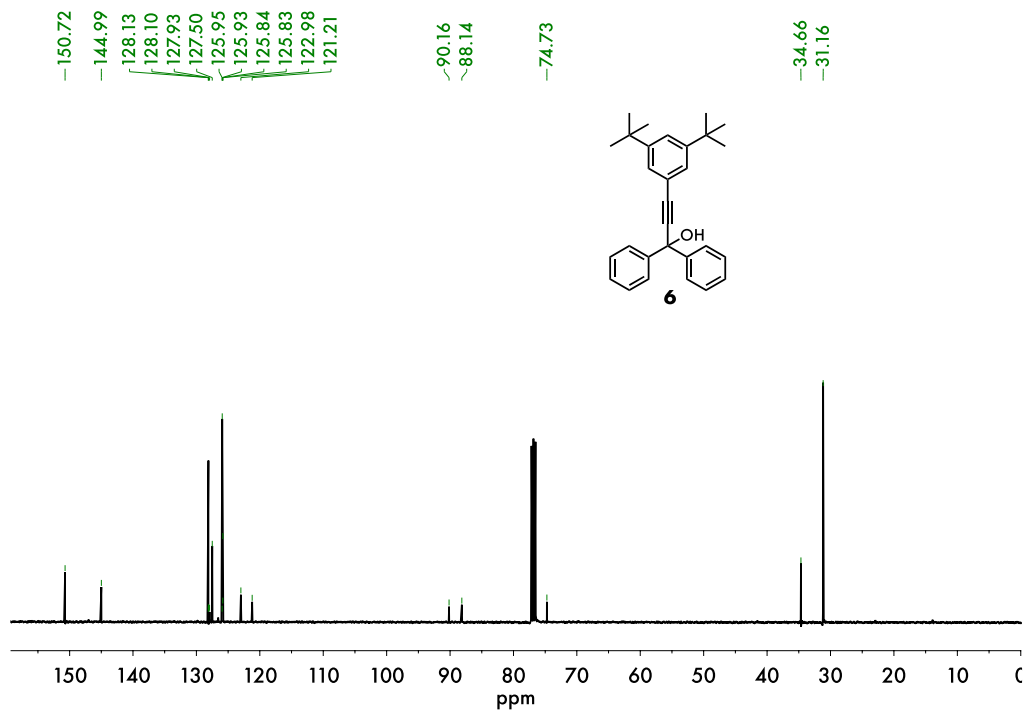


Fig. S10. ¹³C NMR spectrum of **6** (101 MHz, CDCl₃).

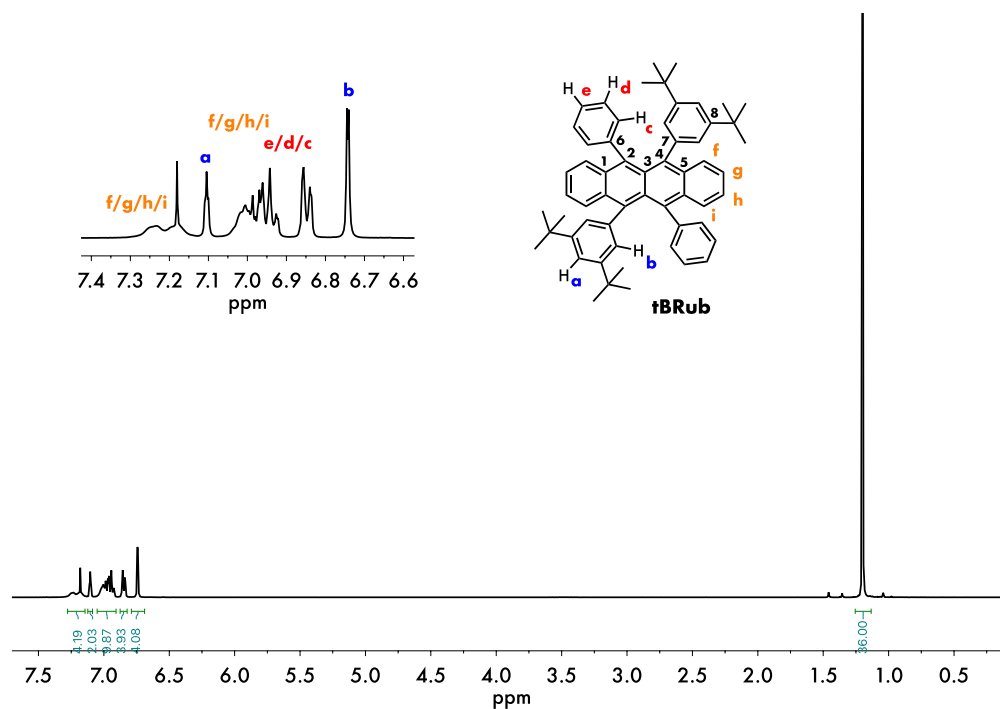


Fig. S11. ^1H NMR spectrum of **tBRub** (400 MHz, CDCl_3).

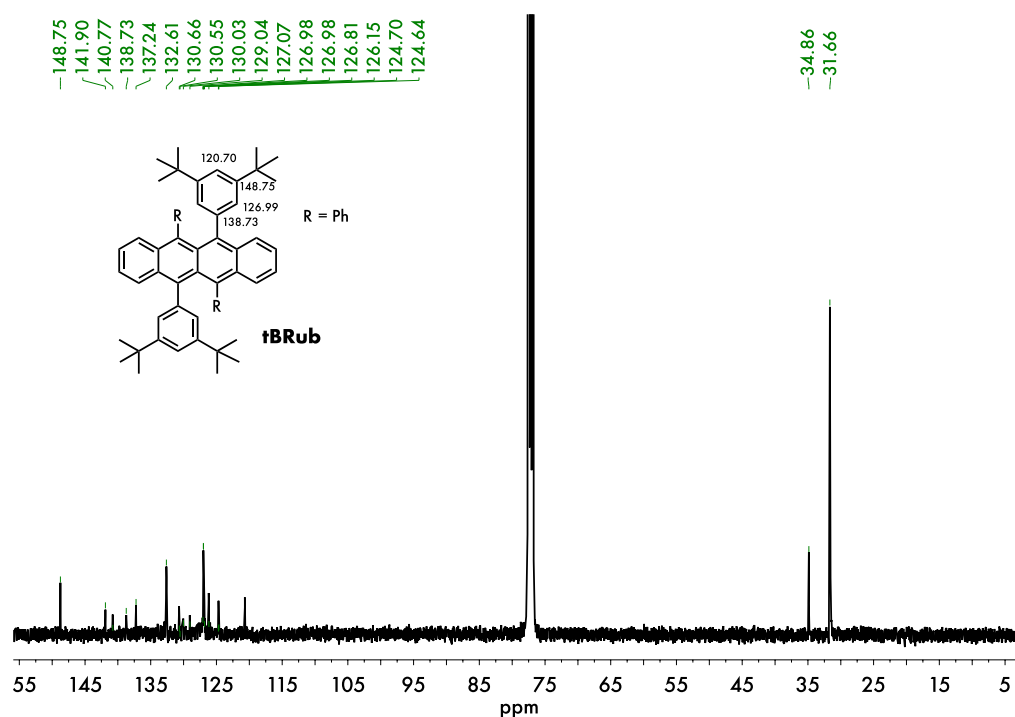


Fig. S12. ^{13}C NMR spectrum of **tBRub** (101 MHz, CDCl_3). The partial assignment of ^{13}C resonances are made by using HSQC and HMBC spectra (see below).

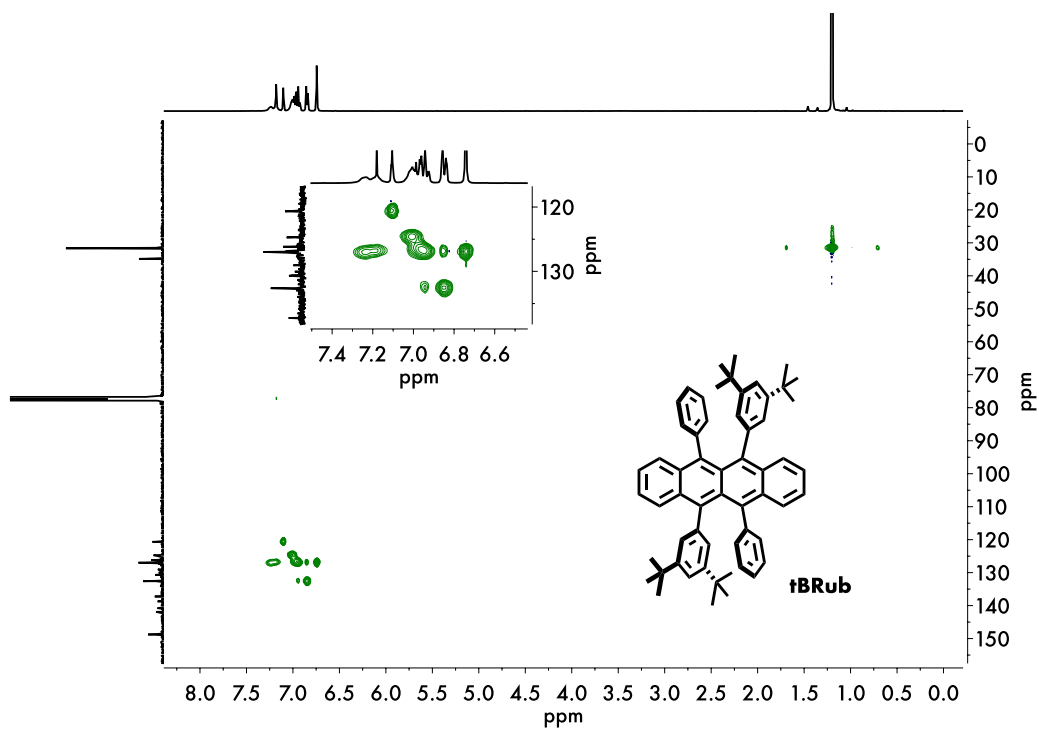


Fig. S13. HSQC spectrum of **tBRub** (400 MHz, CDCl₃).

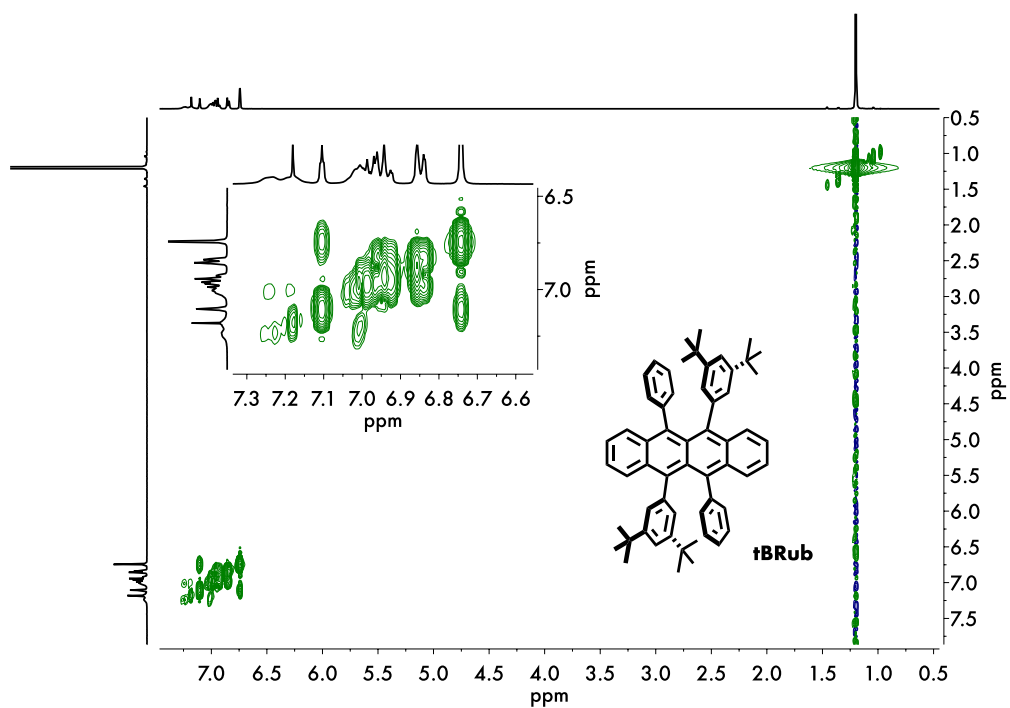


Fig. S14. COSY spectrum of **tBRub** (400 MHz, CDCl₃).

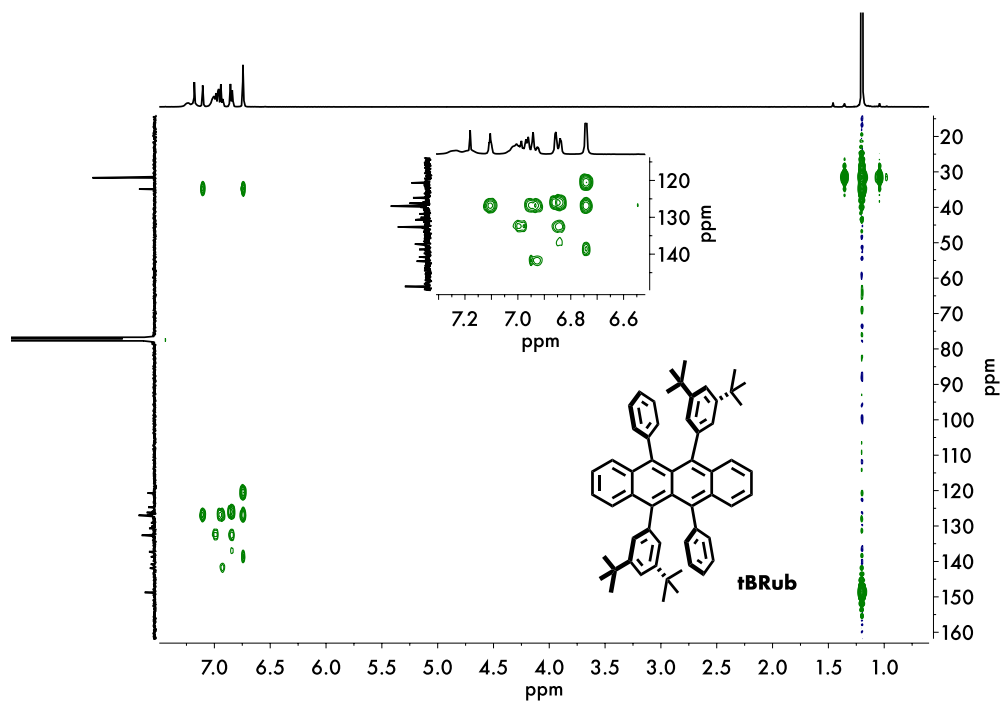
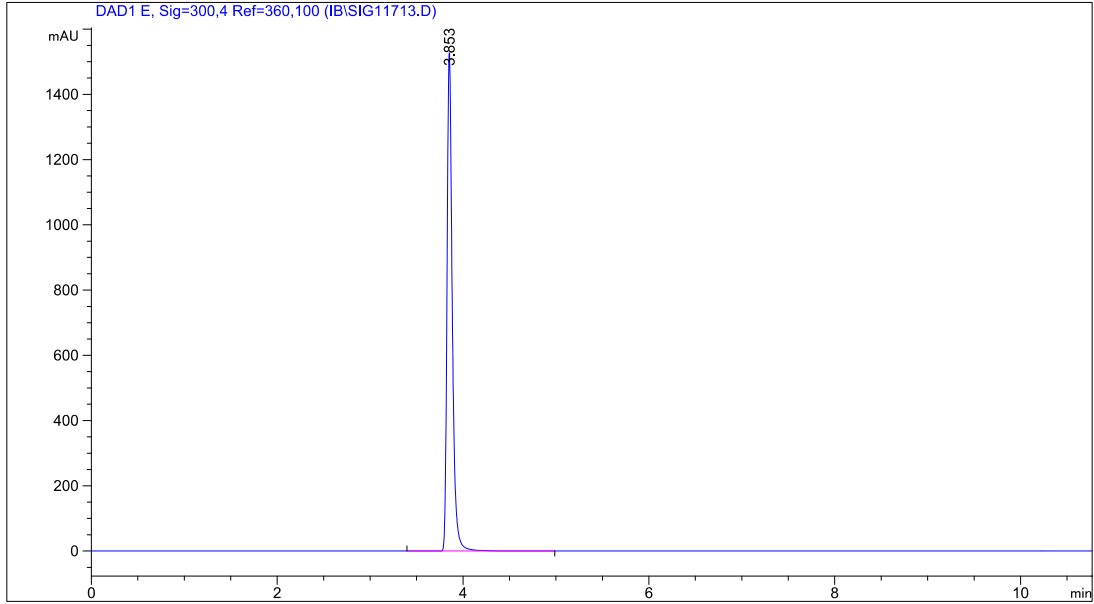


Fig. S15. HMBC spectrum of **tBRub** (400 MHz, CDCl₃).

=====
Acq. Operator :
Acq. Instrument : Instrument 1 Location : -
Injection Date : 2020-01-16 12:52:11 Inj Volume : Manually
Acq. Method : C:\CHEM32\1\METHODS\COLUMN_IB3_TEST.M
Last changed : 2020-01-16 12:18:54
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\COLUMN_IB3_TEST.M
Last changed : 2020-01-16 13:05:03
(modified after loading)
Additional Info : Peak(s) manually integrated



=====
Area Percent Report
=====

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

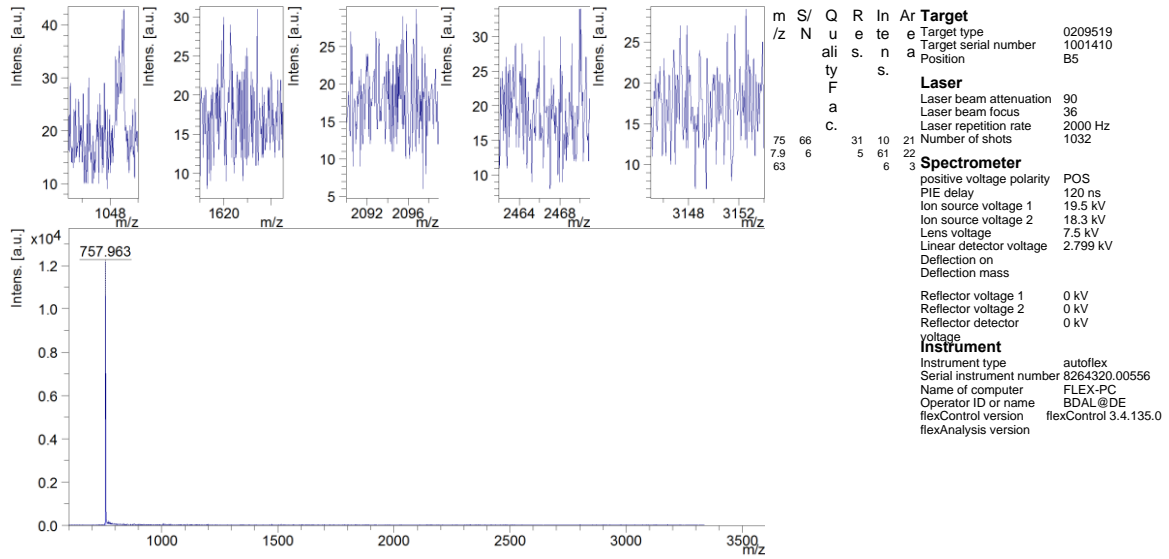
Signal 1: DAD1 E, Sig=300,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.853	BB	0.0623	6020.25000	1517.60022	100.0000

Totals : 6020.25000 1517.60022

=====
*** End of Report ***

Fig. S16. Chromatogram of **tBRub** (column Chiralpak-IB3, eluent-hexane).



Date of Acquisition 2020-01-22T16:04:50.173+00:00
Acquisition method D:\Methods\flexControlMethods\Installation2014_09_08\LP_700-2000_Da_VM2.par
Processing method
File Name D:\Duomenys\EO\EO\IBuRub_B5_10%0_B5\1

Performed by	Viewed by
Date / Sign	Date / Sign

BRUKER DALTONICS
printed 1/22/2020 4:12:34 PM

Fig. S17. MALDI-TOF spectrum of tBRub.

PHOTOPHYSICAL PROPERTIES

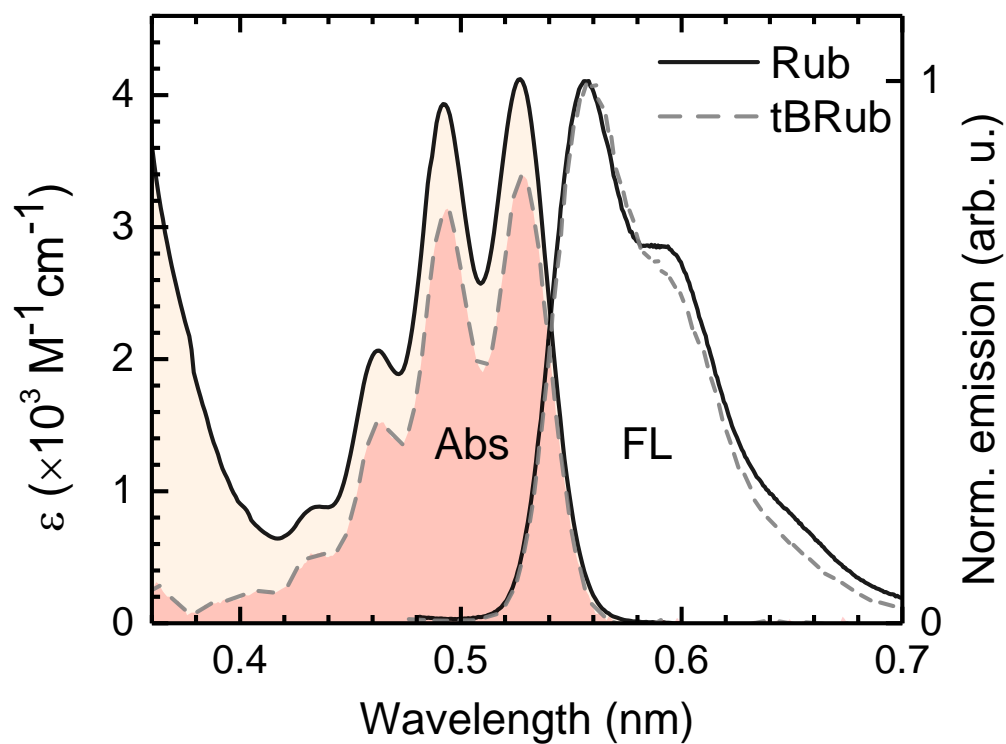


Fig. S18. Absorption and fluorescence spectra of the emitters **Rub** (solid line) and **tBRub** (dashed line) in toluene ($c = 1.0 \times 10^{-5} \text{ M}$).

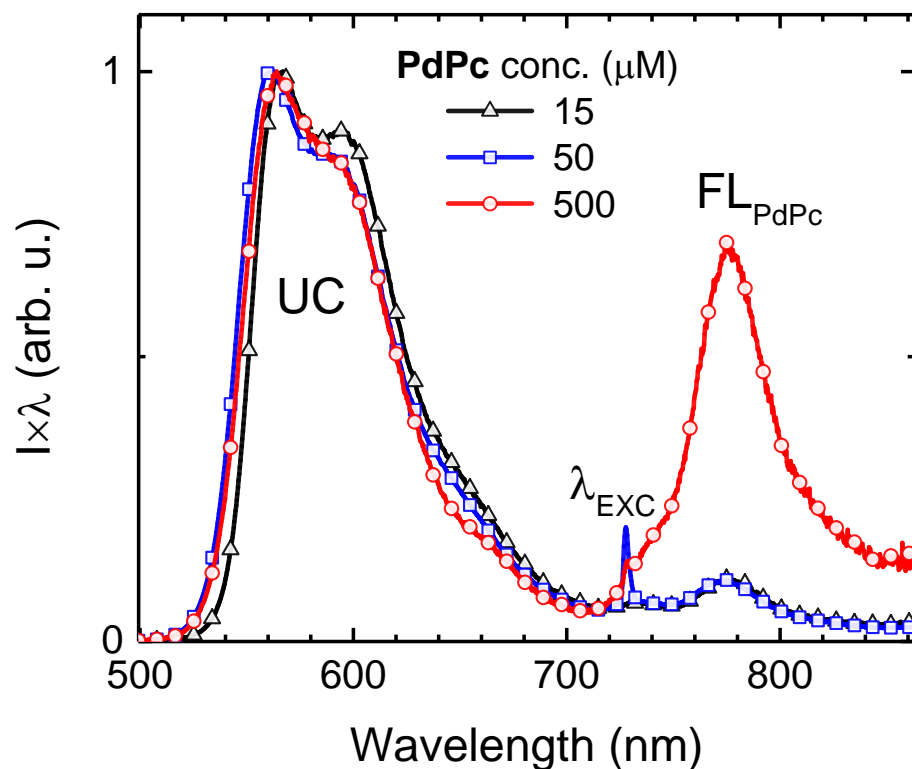


Fig. S19. Normalized UC and FL emission spectra of **Rub:PdPc** solution in toluene at different **PdPc** concentrations (indicated) and fixed **Rub** (18mM) concentration under CW excitation at 730nm. Area under the curves is proportional to the number of photons registered.

The data in Fig. S19 shows that UC emission intensity remains the same and high in respect to that of FL_{PdPc} in the low **PdPc** concentration range 15 - 50 μM . However, at higher concentrations the ratio of UC and FL_{PdPc} intensities drops down indicating enhanced energy back-transfer to sensitizer.

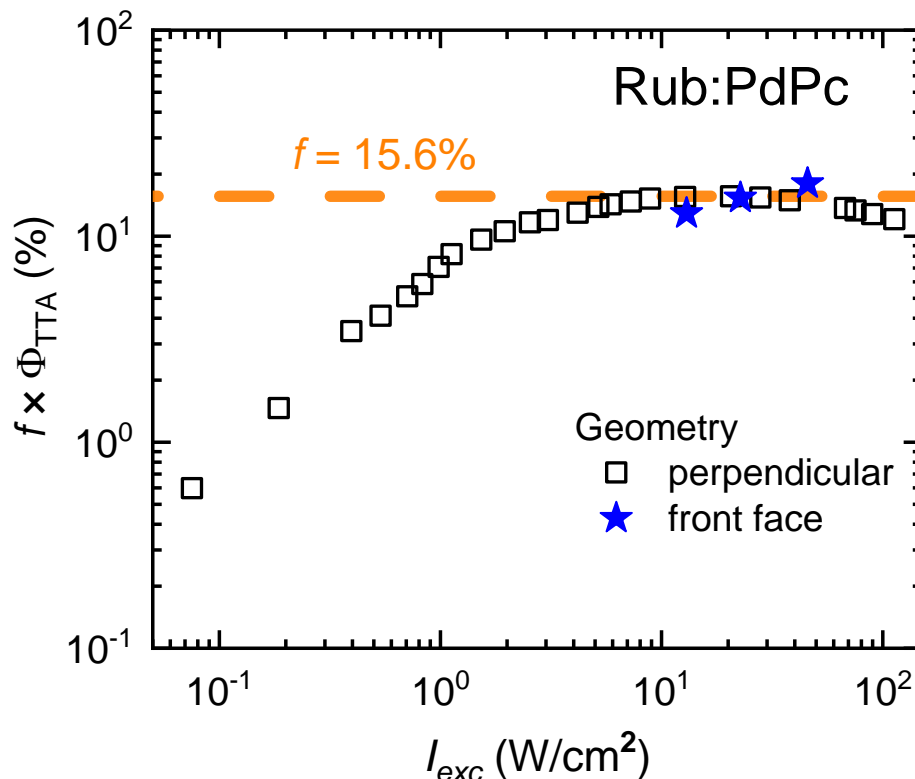


Fig. S20. Excitation dependence of the product $[f \cdot \Phi_{TTA}]$ of **Rub** (18 mM):**PtPc** (15 μ M) system at different excitation-detection geometries (indicated).

Corrections of I_{UC} for the different penetration depth of excitation

Almost 4-fold different molar extinction coefficients of **PdPc** and **PtPc** sensitizers at the UC excitation wavelength of 730 nm caused different excitation penetration depth (d) in the UC solutions

$$d_{PdPc} = \frac{\log(e)}{\varepsilon \times c} = \frac{\log(e)}{1.9 \cdot 10^5 M^{-1} cm^{-1} \times 15 \cdot 10^{-6} M} = 0.15 cm$$

$$d_{PtPc} = \frac{\log(e)}{5 \cdot 10^4 M^{-1} cm^{-1} \times 15 \cdot 10^{-6} M} = 0.58 cm$$

To correct for the different emission collection efficiency of the detector because of the different d , **PtPc** concentration was increased ca. 4 times from 15 μ M to 56 μ M so that $d_{PdPc} = d_{PtPc}$. The correction factor (≈ 4) deduced from UC emission intensity measurements at these two concentrations at $I_{exc} = 100 W/cm^2$ was used then to correct I_{UC} data of **Rub:PtPc** system (see Fig. 6b, main article) to compensate for the reduced collection efficiency.

To find out whether any corrections due to the different d are required to compare I_{UC} and I_{FL} , the following estimations were made. Excitation penetration depth at the FL excitation wavelength of 485 nm (direct excitation of **Rub** emitter) in all the studied rubrene-based UC systems is much smaller in respect to the d in the case of sensitizer excitation at 730 nm

$$d_{Rub} = \frac{\log(e)}{3.3 \cdot 10^3 \text{M}^{-1} \text{cm}^{-1} \times 18 \cdot 10^{-3} \text{M}} = 0.007 \text{cm}$$

Taking into account that $I_{UC} \propto [T_1^{Rub}]^2$ and T_1^{Rub} decay follows that of the **PdPc** sensitizer with $d_{PdPc} = 0.15 \text{cm}$ in **Rub:PdPc** system at 730 nm, I_{UC} signal will emerge from twice as shorter penetration depth as compared to d_{PdPc} , $d_{UC} = d_{PdPc}/2 \approx 0.07 \text{cm}$.

Our thorough measurements clearly demonstrate that in the currently utilized excitation-detection configuration emission collection efficiency of the detector does not change for the $d < 0.08 \text{cm}$, thus enabling to compare I_{UC} and I_{FL} directly without using any corrections.

REFERENCES

- S1. E. A. Safonova, A. G. Martynov, S. E. Nefedov, G. A. Kirakos, Y. G. Gorbunova, A. Y. Tsivadze, *Inorg. Chem.*, **2016**, *55*, 2450-2459.
- S2. Y. Ushitani, Y. Teki, T. Takui, K. Itoh, *Macromolecules*, **1993**, *26*, 6673–6675.