Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information (ESI) for:

Cross-coupling-annulation cascade from *peri*-dibromonaphthalimide to *pseudo*-rylene bisimides

Sabine Seifert, David Schmidt and Frank Würthner*

Universität Würzburg, Institut für Organische Chemie and Center for Nanosystems Chemistry, Am Hubland, 97074 Würzburg, Germany

E-mail: wuerthner@chemie.uni-wuerzburg.de

Table of Contents

1. UV/Vis and fluorescence spectra

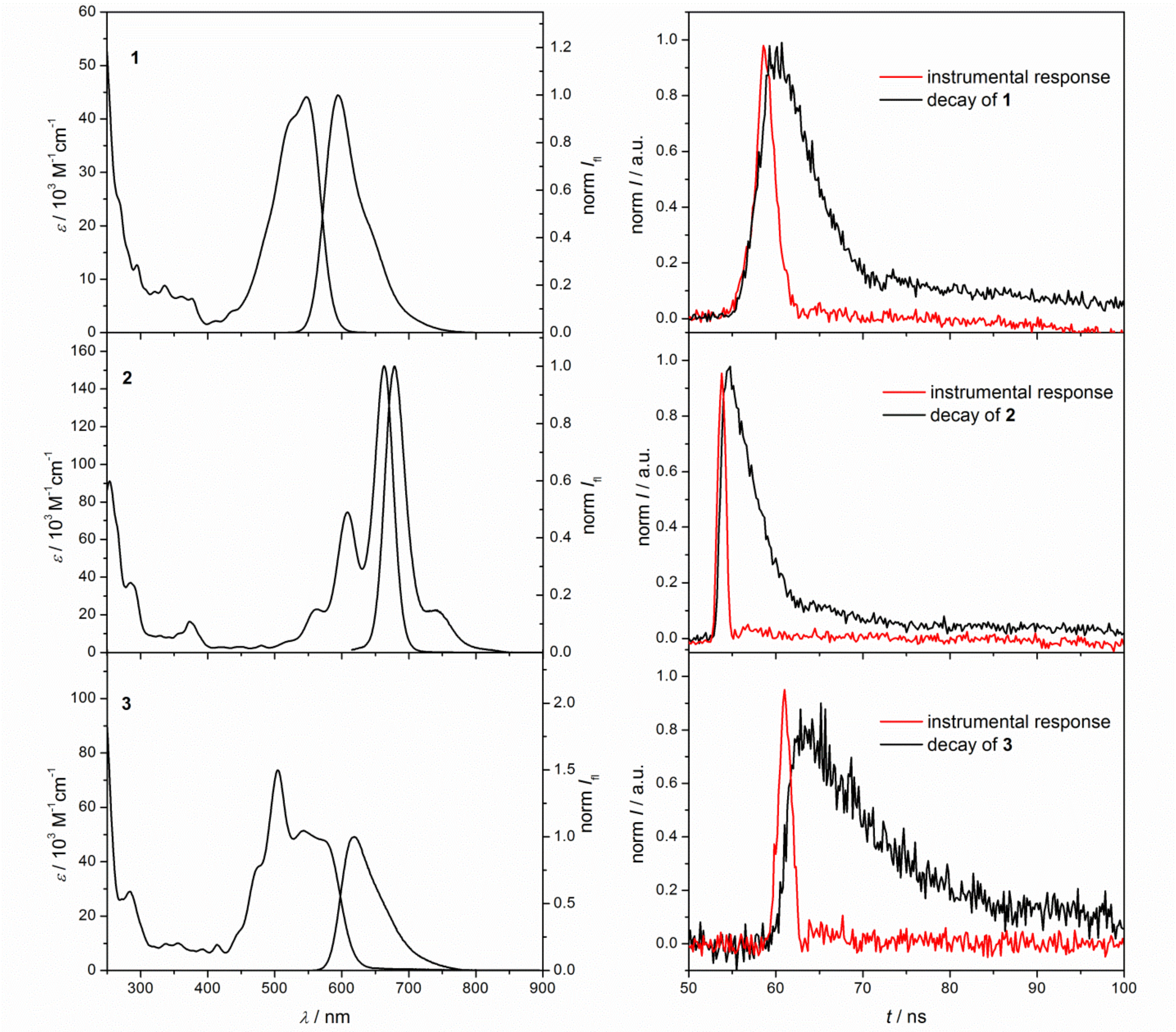

Fig. S1 UV/Vis and steady state fluorescence spectra of **1-3** in CH_2Cl_2 at room temperature (left) and their time-resolved fluorescence decay (right; λ_{ex} = 490 nm, λ_{det} = 598 nm for **1**, λ_{ex} = 649 nm, λ_{det} = 681 nm for **2**, λ_{ex}= 572 nm, λ_{det} = 632 nm for **3**)

Table S1 Summary of the optical properties of compounds **1-3**^{a}

Cpd.	λ_{max}^{abs} [nm]	ε [M^{-1}cm^{-1}]	λ_{max}^{em} [nm]	$\varnothing_{fl}$ [%]^{b}	τ [ns]
1	547	44200	598	79 ± 4	4.87 ± 0.099
2	563, 608, 663	23000, 74600, 152200	681	40 ± 5	4.75 ± 0.008
3	504, 543, 575	73700, 51400, 47700	632	79 ± 5	6.61 ± 0.048

[a] Spectra were measured in dichloromethane at room temperature. [b] Relative fluorescence quantum yields measured by optical dilute method (A<0.05)[S1] by using rhodamine 101 ($\varnothing_{fl}$ = 91.5% in ethanol) or oxazine 1 ($\varnothing_{fl}$ = 15% in ethanol) as standard.[S2] The compounds were excited at different wavelengths and the values with deviations were averaged over 4 different measurements for each compound.

2. DFT calculations

DFT calculations were performed using the Gaussian 09 program package[S3] with B3-LYP[S4] as functional and def2-SVP[S5] as basis set. The structures were geometry optimized, followed by frequency calculations on the optimized structures, which confirmed the existence of minima.

Time-dependent (TD)-DFT calculations were carried out on the optimized structure using the same functional (B3-LYP) and basis set (def2-SVP) as for the geometry optimization. The UV/Vis spectra were simulated using the GaussView 5[S6] visualization software package. A half-width of 0.15 eV was assumed for proper simulation.

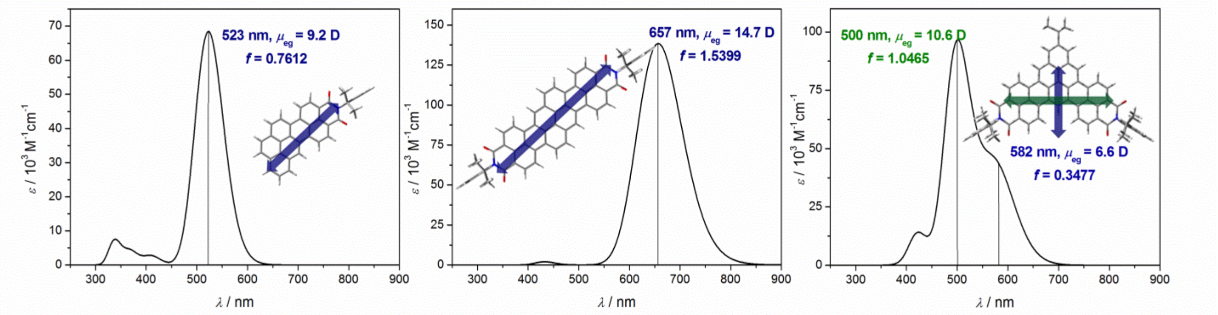

Fig. S2 Calculated UV/Vis spectra of **1**, **2** and **3** (from left to right) with the most prominent transitions and their transition dipole moments (μ_{eg}) as well as oscillator strengths (f) obtained by TD-DFT calculations

3. X-Ray structure analysis

Single-crystal X-ray diffraction data for **1** were collected at 200 K on a Bruker D8 Quest Kappa diffractometer with a Photon100 CMOS detector and multi-layered mirror monochromated $Cu_{K\alpha}$ radiation and that for **2** were collected at 100 K on a Bruker X8APEX-II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structures were solved using direct methods, expanded with Fourier techniques and refined with the Shelx software package.[S7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation on geometrically idealized positions.

Single crystals of **1** suitable for X-ray structural analysis were grown by slow diffusion of n-hexane into a solution of **1** in dichloromethane.

*Crystal data for **1*** ($C_{40}H_{29}NO_2 \bullet CH_2Cl_2$): Mr = 640.57, 0.23 x 0.14 x 0.05 mm^3, triclinic space group $P\bar{1}$, a = 9.1392(2) Å, α = 77.6080(10)°, b = 13.2716(3) Å, β = 76.0260(10)° c = 13.7699(3) Å, γ = 84.9090(10)°, V = 1581.79(6) Å^3, Z = 2, ρ(*calcd)* = 1.345 g·cm^{-3}, μ = 2.145 mm^{-1}, $F_{(000)}$ = 668, $GooF(F^2)$ = 1.035, R_1 = 0.0737, wR^2 = 0.2179 for I>2σ(I), R_1 = 0.0802, wR^2 = 0.2253 for all data, 6207 unique reflections [$\theta \leq$ 72.225°] with a completeness of 99.8% and 486 parameters, 8 restraints.

Single crystals of **2** suitable for X-ray structural analysis were grown by slow diffusion of toluene into a solution of **2** in dichloromethane.

*Crystal data for **2*** ($C_{64}H_{48}N_2O_4 \bullet 2\ C_7H_8 \bullet CH_2Cl_2$): Mr = 1178.23, 0.23 x 0.07 x 0.05 mm^3, monoclinic space group $P2_1/c$, a = 13.3641(12) Å, α = 90°, b = 15.7960(14) Å, β = 112.839(2)° c = 14.8901(13) Å, γ = 90°, V = 2896.9(4) Å^3, Z = 2, ρ(*calcd)* = 1.351 g·cm^{-3}, μ = 0.171 mm^{-1}, $F_{(000)}$ = 1240, $GooF(F^2)$ = 1.035, R_1 = 0.0494, wR^2 = 0.1334 for I>2σ(I), R_1 = 0.0651, wR^2 = 0.1459 for all data, 5776 unique reflections [$\theta \leq$ 26.145°] with a completeness of 100.0% and 420 parameters, 0 restraints.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1497040 (**1**), CCDC 1497041 (**2**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data.request/cif.

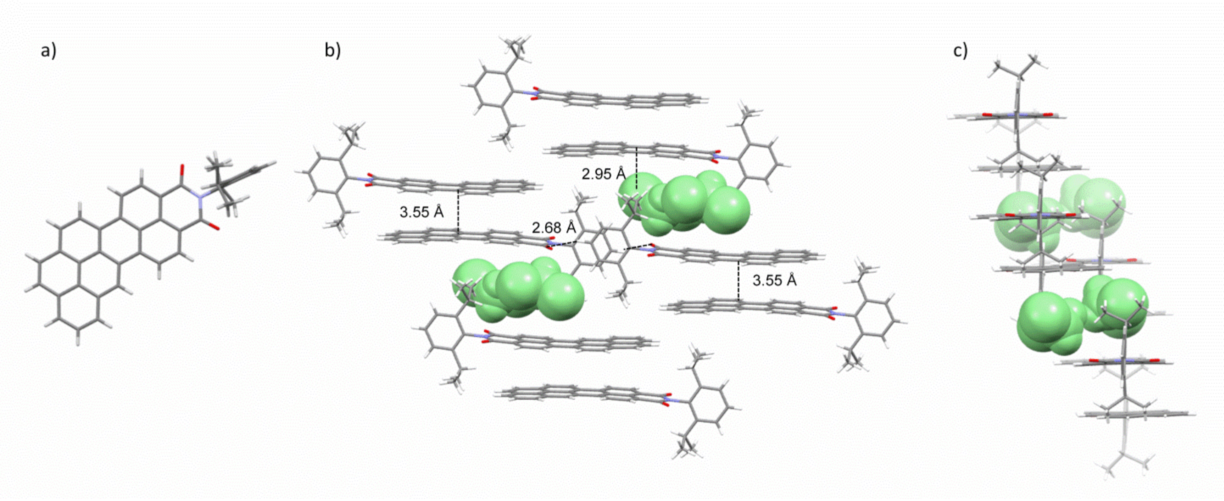

Fig. S3 Molecular structure of **1** in the solid state. a) Top view on the aromatic *π*-surface, b) and c) packing arrangement of **1** in the solid state with included dichloromethane molecules (green)

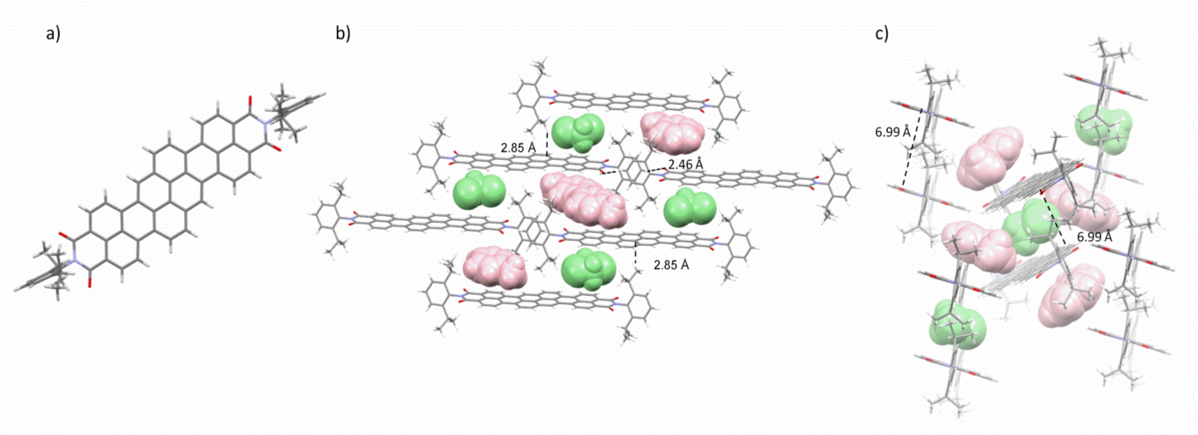

Fig. S4 Molecular structure of **2** in the solid state. a) Top view on the aromatic *π*-surface, b) and c) packing arrangement of **2** in the solid state with included dichloromethane (green) and toluene molecules (pink)

4. NMR spectra

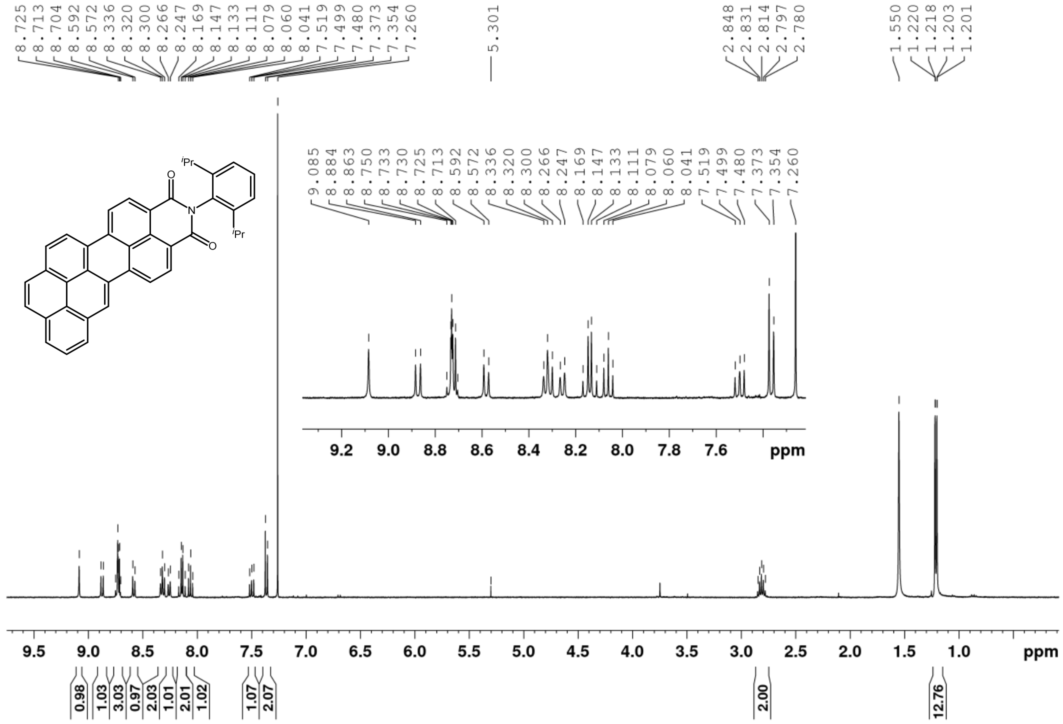

Fig. S5 ^{1}H NMR spectrum of **1** in $CDCl_3$ (400 MHz, 298 K) with residual water peak at 1.55 ppm and dichloromethane peak at 5.30 ppm

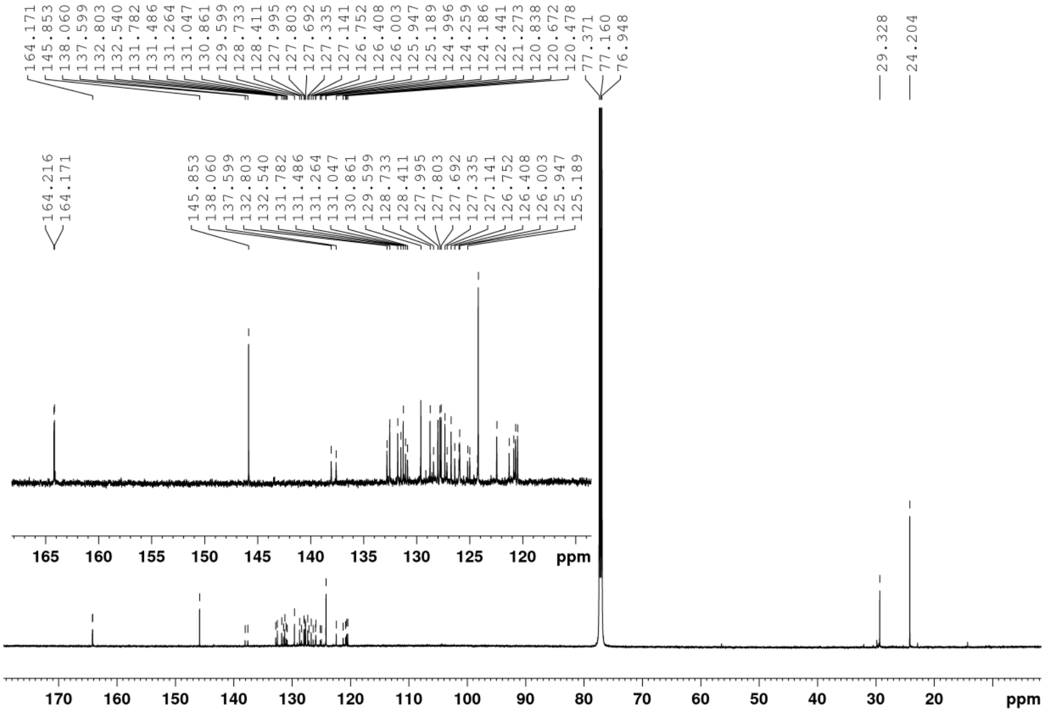

Fig. S6 ^{13}C NMR spectrum of **1** in $CDCl_3$ (151 MHz, 298 K)

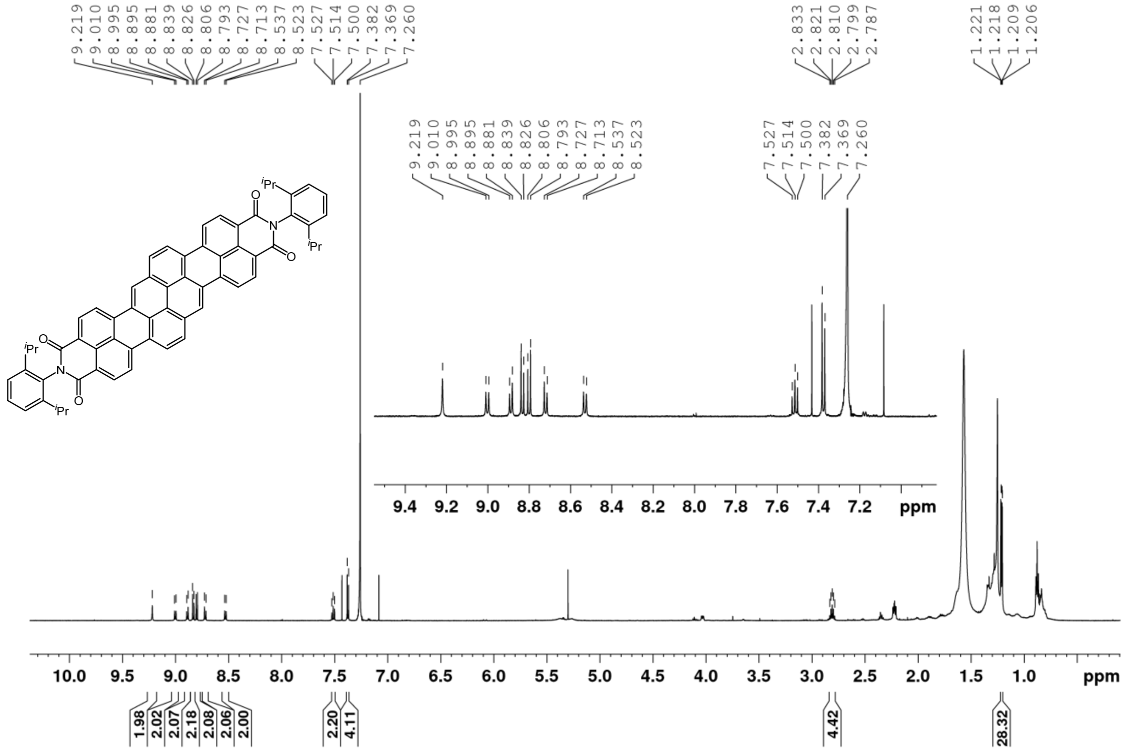

Fig. S7 ^{1}H NMR spectrum of **2** in CDCl$_3$ (600 MHz, 298 K) with solvent impurity (hexane and water) peaks in the aliphatic region

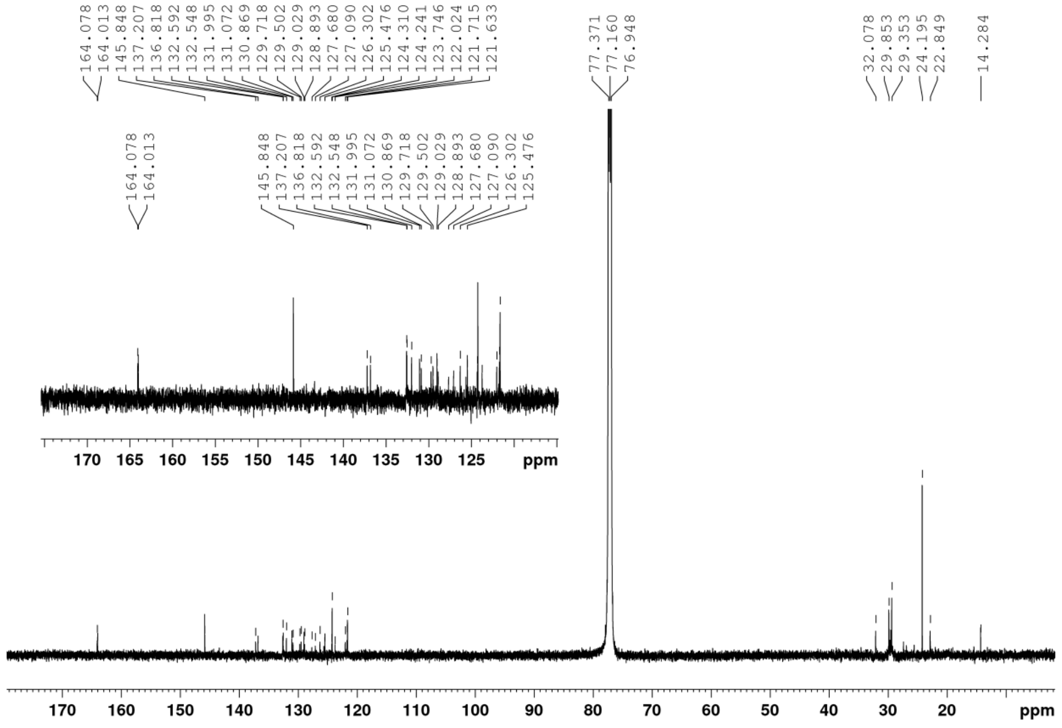

Fig. S8 ^{13}C NMR spectrum of **2** in CDCl$_3$ (151 MHz, 298 K) with solvent impurity (hexane) peaks in the aliphatic region

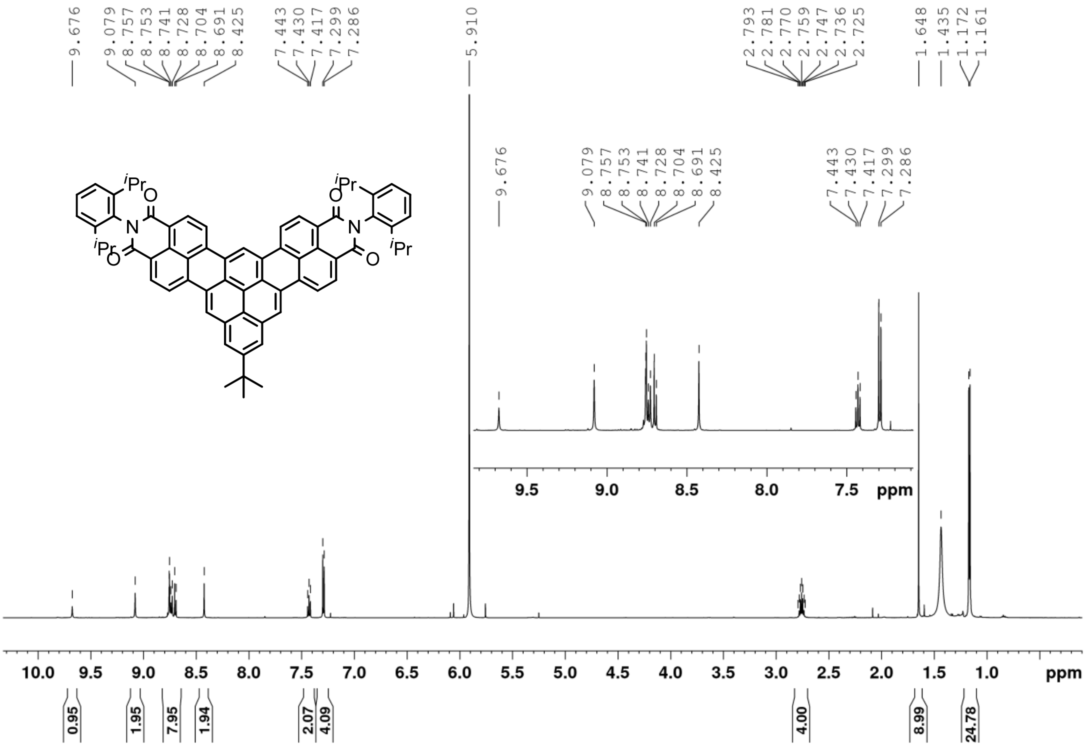

Fig. S9 ^{1}H NMR spectrum of **3** in $C_2D_2Cl_4$ (600 MHz, 345 K) with residual water at 1.44 ppm

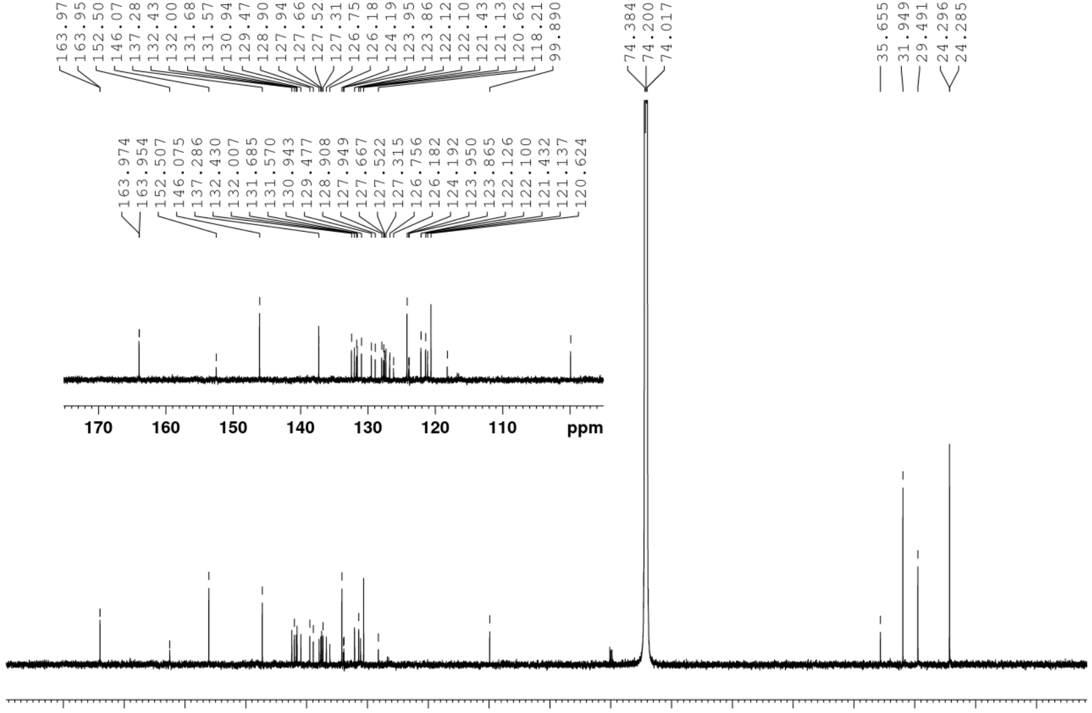

Fig. S10 ^{13}C NMR spectrum of **3** in $C_2D_2Cl_4$ (151 MHz, 345 K)

5. MS spectra

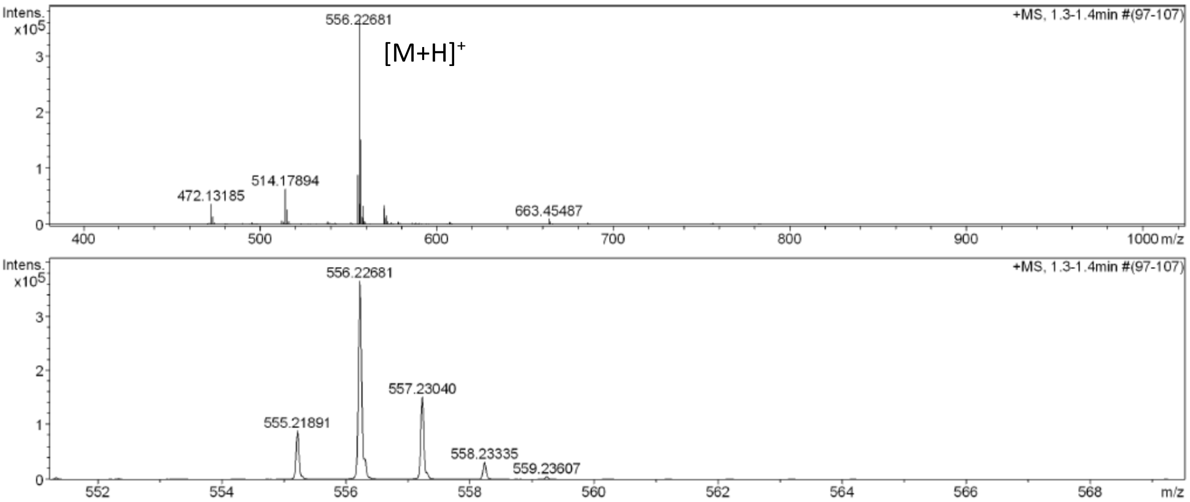

Fig. S11 HRMS (ESI-TOF, pos. mode, acetonitrile/chloroform) spectrum of **1** $[M]^+$ and $[M+H]^+$

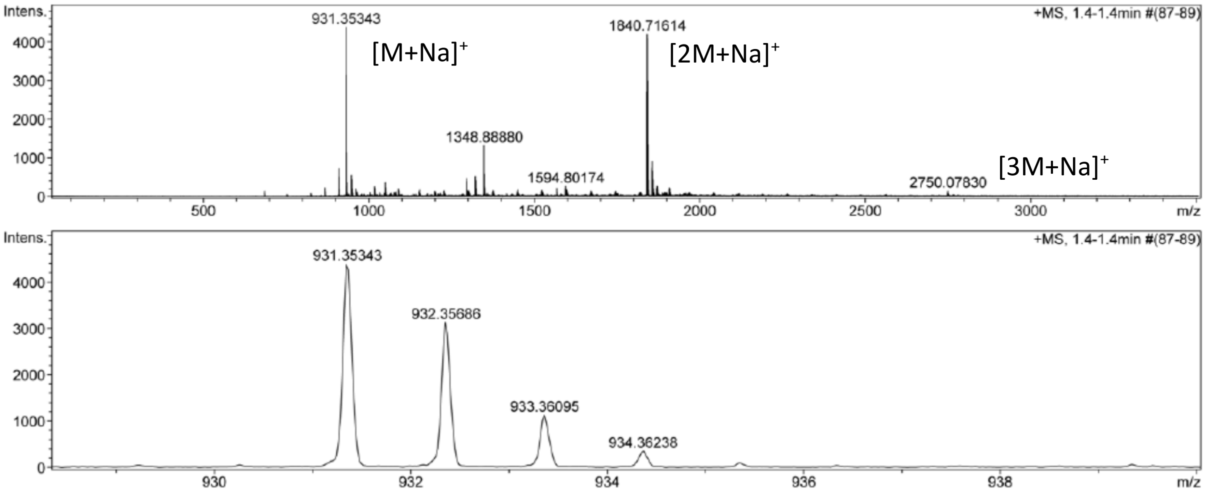

Fig. S12 HRMS (ESI-TOF, pos. mode, acetonitrile/chloroform) spectrum of **2** $[M+Na]^+$

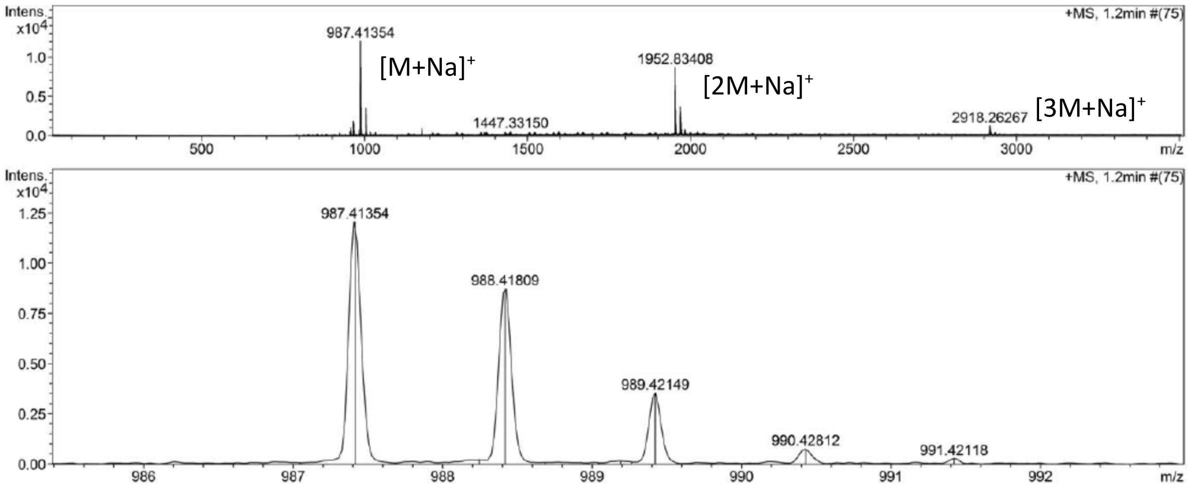

Fig. S13 HRMS (ESI-TOF, pos. mode, acetonitrile/chloroform) spectrum of **3** $[M+Na]^+$

6. References

S1 J. R. Lakowicz, *Principles of Fluorescence Spectroscopy, 2nd ed.,* New York, 1999, 52.

S2 C. Würth, M. Grabolle, J. Pauli, M. Spieles and U. Resch-Genger, *Nat. Protoc.*, 2013, **8**, 1535.

S3 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

S4 (*a*) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; (*c*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

S5 F. Weigand and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.

S6 GaussView, Version 5, R. Dennington, T. Keith, J. Millam, Semichem Inc., Shawnee Mission KS, 2009.

S7 G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112.