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1 General information

All synthetic work was carried out using standard Schlenk techniques under argon atmosphere. Solvents were dried with an MBraun MB-SPS-800 Solvent Purification System and stored over molecular sieves.

The following chemicals were purchased and used as delivered: hexamethylbenzene (99 %, abcr), HBF$_4$·OEt$_2$ (Sigma-Aldrich), N-ethylcarbazole (97 %, Sigma-Aldrich), AgClO$_4$ (99 %, abcr), 10-methylacridone (98 %, TCI), LiAlD$_4$ (98 %, strem chemicals), 1-benzyl-1,4-dihydronicotinamide (>95 %, TCI), 9,10 dihydroanthracene (technical grade, Sigma-Aldrich), NH$_4$PF$_6$ (99 %, acros), ferrocenium hexafluorophosphate (technical grade, Sigma-Aldrich), 1,4-diaminobenzene dihydrochloride (>99%, Sigma-Aldrich).

The synthesis of 3,3'',4,4''-tetramethoxy-o-terphenyl, 3,3''-dimethoxy-3',4'-dimethyl-o-terphenyl (1), 1(BF$_4$)$_2$, 1(PF$_6$)$_2$, 2 and 2(PF$_6$)$_2$ followed the literature procedures. Elemental analyses were carried out at the Microanalytical Laboratory of the University of Heidelberg. NMR spectra were recorded on a Bruker DPX 200, Bruker DRX 200, Bruker Avance II 400 or Bruker AVANCE III 600 system. Solvent resonances were taken as references for all $^1$H NMR spectra. UV-vis spectra were recorded with a Cary 5000 spectrophotometer and cyclic voltammetry (CV) measurements relied on a Metrohm Autolab potentiostate PGSTAT204, ("Bu$_4$N)(PF$_6$) (electrochemical grade (>99.0), Fluka) was employed as supporting electrolyte. Stopped flow measurements were made with an "Applied Photophysics SX 18MV-R". MS-ESI measurements relied on a Bruker microTOF II ESI mass spectrometer.

X-ray crystallography

Suitable crystals for single-crystal structure determination were taken directly from the mother liquor, taken up in perfluorinated polyether oil and fixed on a cryo loop. Full shells of intensity data were collected at low temperature with a Nonius Kappa CCD diffractometer (Mo-K$_\alpha$ radiation, sealed X-ray tube, graphite monochromator) for compound (2+2H)(PF$_6$)$_2$, and Bruker D8 Venture, dual source (Mo- or Cu-K$_\alpha$ radiation, microfocus X-ray tube, Photon III detector) for all other compounds. Data were processed with the standard Nonius and Bruker (SAINT, APEX3) software package.$^a$

[1] Linyi Zhai, Ruchi Shukla, Shiriya H. Wadumethrige, Rajendra Rathore, J. Org. Chem. 2010, 75, 4748–4760.
[2] U. Wild, O. Hübner, L. Greb, M. Enders, E. Kaifer, H.-J. Himmel, Eur. J. Org. Chem. 2018, 5910–5915.
[3] U. Wild, S. Federle, A. Wagner, E. Kaifer, H.-J. Himmel, Chem. Eur. J. 2016, 22, 11971–11976.
[4] J. Hornung, O. Hübner, E. Kaifer, H.-J. Himmel*, RSC Advances 2016, 6, 39323-39329
[5] a) DENZO-SMN, Z. Otwinowski & W. Minor, Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol. 1997, 276, Eds C. W. Carter. R. M. Sweet, Academic Press.; b) SAINT, Bruker AXS GmbH, Karlsruhe, Germany 2016.
Multiscan absorption correction was applied using the SADABS program.\footnote{[6]} The structures were solved by intrinsic phasing\footnote{[7]} and refined using the SHELXTL software package (Version 2014\slash 6 and 2018\slash 3).\footnote{[8]} Graphical handling of the structural data during solution and refinement were performed with OLEX2.\footnote{[9]} All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms bound to carbon were input at calculated positions and refined with a riding model. Hydrogen atoms bound to nitrogen were located in difference Fourier syntheses and refined, either fully or with appropriate distance and/or symmetry. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre (CCDC No. 2013656 for 1(ClO$_4$)$_2$, 2013653 for (2+2H)(PF$_6$)$_2$, 2013654 for 3, 2013652 for 3(PF$_6$)$_2$, 2013655 for (3+H)(PF$_6$)$_2$, 2013657 for (3+2H)(PF$_6$)$_2$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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\bibitem{7} a) G. M. Sheldrick, SHELXT, \textit{Program for Crystal Structure Solution}, University of Göttingen, Germany 2014-2018; b) G. M. Sheldrick, Acta Cryst. \textbf{2015}, \textit{A71}, 3.
\bibitem{8} a) G. M. Sheldrick, \textit{SHELXL-20xx}, University of Göttingen and Bruker AXS GmbH, Karlsruhe, Germany 2012-2018; b) W. Robinson, G. M. Sheldrick in: N. W. Isaaks, M. R. Taylor (eds.) "Crystallographic Computing 4", Ch. 22, IUCr and Oxford University Press, Oxford, UK, 1988; c) G. M. Sheldrick, Acta Cryst. \textbf{2008}, \textit{A64}, 112; (d) G. M. Sheldrick, Acta Cryst. \textbf{2015}, \textit{C71}, 3.
\bibitem{9} O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program, J. Appl. Cryst. \textbf{2009}, \textit{42}, 339.
\end{thebibliography}
2 Synthesis of new compounds

Compound 1(ClO₄)₂

130 mg (0.245 mmol) of 1 and 99 mg (0.478 mmol) of AgClO₄ were dissolved in 20 ml CH₃CN and the reaction mixture stirred for a period of 45 min at room temperature. Then the reaction is filtrated and the solvent removed in vacuo. The solid residue is washed several times with Et₂O. For further purification the CH₃CN solution was layered by Et₂O. The microcrystalline precipitate, formed over a period of several days, was washed several times with Et₂O and dried in vacuo to give 150 mg (0.206 mmol, 86% yield) of 1(ClO₄)₂. Elemental analysis calcd. (%) for C₂₆H₅₀N₁₂Cl₂O₆ (729.66 g·mol⁻¹): C 42.80, H 6.91, N 23.04; found C 42.64, H 6.97, N 23.76. ¹H NMR (600.13 MHz, CD₃CN, 295.0 K): δ = 5.15 (s, 2 H, CH), 2.88 (s, 48 H, CH₃) ppm. ¹³C NMR (150.92 MHz, CD₃CN, 295.1 K): δ = 167.62, 157.26 (C₆), 103.46 (CH), 40.96 (CH₃) ppm. MS (ESI, CH₃CN): m/z (%) = 265 (100) [1²⁺], 244 (60) [1H-N(CH₃)₆]²⁺, 629 (39) [1(ClO₄)]⁺. Crystal data: C₂₆H₅₀Cl₂N₁₂O₆·PF₆; Mr = 729.68, 0.12 × 0.113 × 0.107 mm⁻³, monoclinic, space group P2(1)/n, a = 7.8129(17), b = 17.529(2), c = 13.203(2) Å, β = 93.468(9), V = 1804.9(6) Å³, Z = 2, d_calc = 1.343 g cm⁻³, Mo-Kα radiation (λ = 0.71073 Å), T = 100 K, θ_range 1.933° to 28.495°, Reflections measd. 45272, indep. 4581, R_int = 0.0583, Final R indices [I > 2σ(I)]: R₁ = 0.0429, wR₂ = 0.1091.

NMR experiment: 1 + (1+2H)(PF₆)₂

In an NMR tube, compound 1 (3.588 mg, 6.76·10⁻³ mol) and (1+2H)(PF₆)₂ [¹] (5.400 mg, 6.56·10⁻³ mol) were dissolved in 0.45 ml CD₃CN. After 10 min at room temperature, the solution was studied by NMR spectroscopy. ¹H NMR (399.89 MHz, CD₃CN, 294.6 K): δ = 5.84 (s, 2 H, CH_arom), 2.70 (s, 48 H, CH₃) ppm.

Compound (2+2H)(PF₆)₂

A solution of ammonium hexafluorophosphate (158 mg, 0.96 mmol) in CH₃CN (4 ml) is added to a solution of compound 2 (152 mg, 0.50 mmol) in CH₃CN (3 ml). The reaction mixture is stirred for 1 h at 50 °C and additional 18 h at room temperature. The solvent is removed in vacuo and the solid residue re-dissolved in CH₃CN (3 ml). After addition of charcoal the solution is filtered over celite. The solution is concentrated by removal of half of the solvent and then layered with diethyl ether. Compound (2+2H)(PF₆)₂ is obtained as colorless crystals in a yield of 196 mg (0.33 mmol, 68%), that are structurally characterized by single-crystal X-ray diffraction. Elemental analysis calcd. (%) for C₁₆H₃₀N₆F₁₂P₂ (596.38 g·mol⁻¹): C 32.22, H 5.07, N 14.09, found C 32.43, H 5.37, N 14.13. ¹H NMR (399.98 MHz, CD₃CN, 295.4 K): δ = 7.08 (m, 4 H, CH_arom), 2.95 (s, 24 H, CH₃) 7.96 ppm (2 H, NH). ¹³C NMR (100.56 MHz, CD₃CN, 295.9 K): δ = 158.87, 135.27, 122.88, 40.38 ppm.

[¹] A. Peters, E. Kaifer, H.-J. Himmel, Eur. J. Org. Chem. 2008, 5907–5914
NMR experiment: $2 + (2+2H)(PF_6)_2$

In an NMR tube, compound 2 (0.780 mg, $2.56\times10^{-6}$ mol) and $(2+2H)(PF_6)_2$ (1.536 mg, $2.57\times10^{-6}$ mol) were dissolved in 0.5 ml CD$_3$CN. After 10 min at room temperature, the solution was studied by NMR spectroscopy. Attempts to obtain crystals by concentrating the solution to 0.1 ml, layering the solution with diethyl ether and storing it at $-21 \, ^\circ C$ failed. $^1$H NMR (399.89 MHz, CD$_3$CN, 295.3 K): $\delta = 6.61$ (m, 4 H, CH$_{arom}$), 2.70 ppm (s, 24 H, CH$_3$).

1,4-Bis-(N,N'-dimethylethleneguanidino)-benzene, 3

1,3-dimethyl-2-imidazolidinone (2.9 mL, 25 mmol) is dissolved in chloroform (50 ml) oxalylchloride (10.75 ml, 135 mmol) added while stirring. Subsequently, the reaction mixture is heated to reflux for 18 h. Then, the solvent is removed in vacuo and the remaining solid washed with diethyl ether (2 times with portions of 20 ml). The resulting chloroformamidinium chloride is dissolved in acetonitrile (20 ml). This solution is added to a suspension of p-phenylenendiamine-2HCl (1.81 g, 10 mmol) and triethylamine (10 ml, 71.25 mmol) in acetonitrile (30 ml) at -5 °C. After completion of the addition, the reaction mixture is stirred for 5 h at 0 °C. The solvent is removed in vacuo and the remaining solid re-dissolved in aqueous HCl (5%). Once all of the residue is solved, aqueous NaOH (40%) is added. The resulting mixture is extracted with dichloromethane. The organic phases are dried over K$_2$CO$_3$ and the solvent is removed in vacuo. The crude product was re-crystallized from hot acetonitrile. Compound 3 is obtained as a beige solid in a yield of 2.32 g (7.72 mmol, 77.2%). Crystals suitable for structural characterization by single crystal X-ray diffraction are grown from acetonitrile layered by petroleum ether. Elemental analysis calcd. (%) for C$_{16}$H$_{24}$N$_6$ (300.32 g·mol$^{-1}$): C 63.97, H 8.05, N 27.98; found C 63.82, H 7.76, N 28.01. $^1$H NMR (399.89 MHz, CD$_3$CN, 295.4 K): $\delta = 6.56$ (m, 4 H, CH$_{arom}$), 3.19 (s, 8 H, CH$_2$), 2.54 ppm (s, 12 H, CH$_3$). $^{13}$C NMR (100.56 MHz, CD$_3$CN, 295.9 K): $\delta = 155.73$, 143.88, 122.65, 48.90, 35.24 ppm.

Compound 3(PF$_6$)$_2$

Ferroenium hexafluorophosphate (214 mg, 0.62 mmol) and compound 3 (102 mg, 0.339 mmol) are dissolved in 12 ml dry dichloromethane. The reaction mixture is stirred at room temperature for 3h. The solvent is removed in vacuo and the yellow-brown residue washed three times with diethyl ether. The residue is re-dissolved in acetonitrile and layered with diethylether to obtain 90 mg (0.15 mmol, 48%) of an orange crystalline solid as product. Elemental analysis calcd. (%) for C$_{16}$H$_{24}$NeF$_{12}$P$_2$ (590.35 g·mol$^{-1}$): C 32.55, H 4.10, N 14.24; found C 32.23, H 4.35, N 14.17. $^1$H NMR (399.89 MHz, CD$_3$CN, 294.8 K): $\delta = 7.17$ (m, 4 H, CH$_{arom}$), 3.94 (s, 8 H, CH$_2$), 2.83 ppm (s, 12 H, CH$_3$). $^{13}$C NMR (100.56 MHz, CD$_3$CN, 295.9 K): $\delta = 166.07$, 162.39, 49.96, 32.82 ppm.
A solution of ammonium hexafluorophosphate (140 mg, 0.85 mmol) in CH₃CN (2 ml) is added to a solution of compound 3 (144 mg, 0.48 mmol) in CH₃CN (3 ml). The reaction mixture is stirred for 1 h at 50 °C and additional 18 h at room temperature. The solvent is removed in vacuo and the solid residue re-dissolved in CH₃CN (3 ml). After addition of charcoal the solution is filtered over celite. The solution is concentrated by removal of half of the solvent and then layered with diethyl ether. One obtains (3+2H)(PF₆)₂ as colorless crystals in a yield of 205 mg (0.34 mmol, 72%), that are structurally characterized by single-crystal X-ray diffraction. Elemental analysis calcd. (%) for C₁₆H₂₆N₆F₁₂P₂ (592.35 g mol⁻¹): C 32.44, H 4.42, N 14.19; found C 32.56, H 4.76, N 14.26. ¹H NMR (399.89 MHz, CD₃CN, 295.3 K): δ = 7.21 (m, 4 H, CH arom), 3.72 (s, 8 H, CH₂), 2.78 (s, 12 H, CH₃) 7.92 ppm (2 H, NH). ¹³C NMR (100.56 MHz, CD₃CN, 295.9 K): δ = 157.11, 134.52, 124.88, 49.47, 34.70 ppm.

NMR experiment: 3 + (3+2H)(PF₆)₂

In an NMR tube, compound 3 (0.764 mg, 2.54·10⁻⁶ mol) and (3+2H)(PF₆)₂ (1.504 mg, 2.54·10⁻⁶ mol) are dissolved in 0.5 ml CD₃CN. After 10 min at room temperature the solution was studied by NMR spectroscopy. Then the solution is concentrated to 0.1 ml and the solution layered with diethyl ether. One obtains (3+H)(PF₆) as colorless crystals that are structurally characterized by single-crystal X-ray diffraction. ¹H NMR (399.89 MHz, CD₃CN, 295.3 K): δ = 6.89 (m, 4 H, CH arom), 3.46 (s, 8 H, CH₂), 2.66 (s, 12 H, CH₃) 7.92 ppm (2 H, NH).
3 Analytical data for new compounds

NMR spectra

$^1$H NMR spectrum (399.89 MHz, CD$_3$CN, 295.4 K) for compound (2+2H)(PF$_6$)$_2$

![1H NMR spectrum](image)

$^{13}$C NMR spectrum (100.56 MHz, CD$_3$CN, 295.9 K) for compound (2+2H)(PF$_6$)$_2$

![13C NMR spectrum](image)
$^1$H NMR spectrum (399.89 MHz, CD$_3$CN, 295.4 K) of compound 3

$^{13}$C NMR spectrum (100.56 MHz, CD$_3$CN, 295.9 K) of compound 3
$^1$H NMR spectrum (399.89 MHz, CD$_3$CN, 294.8 K) of compound $3$(PF$_6$)$_2$

$^{13}$C NMR spectrum (100.56 MHz, CD$_3$CN, 295.1 K) of compound $3$(PF$_6$)$_2$
$^1$H NMR spectrum (399.89 MHz, CD$_3$CN, 295.3 K) of compound (3+2H)(PF$_6$)$_2$

$^{13}$C NMR spectrum (100.56 MHz, CD$_3$CN, 295.9 K) for compound (3+2H)(PF$_6$)$_2$
$^1$H NMR spectrum (399.89 MHz, CD$_3$CN, 298.2 K) for compound (2+H)(PF$_6$)$_2$ (1:1 mixture of 2 + (2+2H)(PF$_6$)$_2$)

$^{13}$C NMR spectrum (100.56 MHz, CD$_3$CN, 295.9 K) for compound (2+H)(PF$_6$)$_2$ (1:1 mixture of 2 + (2+2H)(PF$_6$)$_2$)
\(^1\)H NMR spectrum (399.89 MHz, CD\(_3\)CN, 298.1 K) for compound (3+H)(PF\(_6\))

\(^1\)H NMR spectrum (399.89 MHz, CD\(_3\)CN, 294.8 K) for compound 2(PF\(_6\))\(_2\) with 10 eq. HBF\(_4\)·OEt\(_2\) after 30 min, 298 K
\(^1\text{H NMR spectra (399.89 MHz, CD}\textsubscript{3}\text{CN, 295.4 K) for compound 1, (1+2H)(PF}_6)_2, and 1:1 mixtures of 1 + (1+H)(PF}_6)_2.\)

\begin{itemize}
  \item \textbf{1}
  \item \textbf{(1+2H)}\textsuperscript{2+}
  \item mixture of 1 eq. 1 + 1 eq. (1+2H)\textsuperscript{2+}
  \item * traces of 1\textsuperscript{2+}
\end{itemize}

\begin{itemize}
  \item Chemical Shift (ppm)
  \item CD\textsubscript{3}CN
\end{itemize}

\begin{itemize}
  \item 7 6 5 4 3 2
  \item \textbf{compound 2}
  \item \textbf{compound 2+H}\textsuperscript{+}
  \item \textbf{compound 2+2H}\textsuperscript{+}
\end{itemize}

\(^1\text{H NMR spectra (399.89 MHz, CD}\textsubscript{3}\text{CN, 295.4 K) for compound 2, (2+H)(PF}_6) and (2+2H)(PF}_6)_2\)
$^1$H NMR spectra (399.89 MHz, CD$_3$CN, 295.4 K) for compound 3, (3+H)(PF$_6$) and (3+2H)(PF$_6$)$_2$
UV-vis spectra in CH$_3$CN solution

- compound 2
- compound 2(PF$_6$)$_2$
- compound (2+2H)(PF$_6$)$_2$
- compound 3
- compound 3(PF$_6$)$_2$
- compound (3+2H)(PF$_6$)$_2$
CV curves

CV curves (CH$_3$CN, Ag/AgCl reference electrode, 0.1 M $N(\eta^3$-Bu)$_4$(PF$_6$) as supporting electrolyte, scan speed 100 mV·s$^{-1}$) for the two compounds 2 and 3 measured in oxidation direction. Potentials given vs. Fc/Fc$^+$. 

- **Compound 2**

- **Compound 3**
### Details of the crystal structure determinations

|                     | \((2+2H)(PF_6)_2\) | 3 | 3\((PF_6)_2\) | \((3+H)(PF_6)\) | \((3+2H)(PF_6)_2\) |
|---------------------|--------------------|---|---------------|-----------------|-------------------|
| CCDC-No. formula    | \(2013653\)        | \(2013654\)      | \(2013652\)     | \(2013655\)      | \(2013657\)       |
| CCDC-No. formula    | \(C_{16}H_{30}Ne_2P_{2}F_{12}\) | \(C_{16}H_{24}Ne_6\) | \(C_{16}H_{24}Ne_2P_{2}F_{12}\) | \(C_{16}H_{26}NePF_6\) | \(C_{16}H_{26}NeF_2P_{2}\) |
| crystal system      | monoclinic         | monoclinic       | monoclinic      | orthorhombic     | monoclinic        |
| space group         | \(P 2_{1}/c\)     | \(P 2_{1}/c\)   | \(P 2_{1}/c\)  | \(P b c a\)      | \(P 2_{1}/c\)     |
| \(a\) /Å            | 10.724(2)          | 8.0529(7)        | 6.0211(2)       | 9.9054(7)        | 7.5715(2)         |
| \(b\) /Å            | 8.9420(18)         | 13.0270(11)      | 22.0229(8)      | 13.5468(9)       | 20.1691(5)        |
| \(c\) /Å            | 12.887(3)          | 8.3789(7)        | 8.7572(3)       | 29.713(2)        | 8.3901            |
| \(\alpha\) /°       | 90                 | 90               | 90              | 90              | 90                |
| \(\beta\) /°        | 99.47(3)           | 112.935(3)       | 104.959(1)      | 90              | 116.291(1)        |
| \(\gamma\) /°       | 90                 | 90               | 90              | 90              | 90                |
| \(V\) /Å³           | 1219.0(4)          | 809.50(12)       | 1121.87(7)      | 3987.0(5)        | 1148.72(5)        |
| \(Z\)               | 2                  | 2                | 2               | 8               | 2                 |
| \(M_r\)             | 596.4              | 300.41           | 590.35          | 446.39          | 592.37            |
| \(F_{000}\)         | 4788               | 324              | 600             | 1856            | 604.0             |
| \(d_c\) /Mg·m⁻³     | 1.6250             | 1.232            | 1.748           | 1.487           | 1.713             |
| \(\mu\) /mm⁻¹       | 0.288              | 0.078            | 0.313           | 0.208           | 0.306             |
| max., min.          |                    |                  |                 |                 |                   |
| transmission factors |                    |                  |                 |                 |                   |
| X-radiation, \(\lambda\) /Å | Mo-K\(\alpha\), 0.71073 | Mo-K\(\alpha\), 0.71073 | Mo-K\(\alpha\), 0.71073 | Mo-K\(\alpha\), 0.71073 | Mo-K\(\alpha\), 0.71073 |
| data collect. temp. /K | 120               | 100              | 100             | 100             | 100               |
| \(\theta\) range /°  | 2.983 to 28.490    | 2.746 to 27.097  | 2.579 to 28.998 | 2.47 to 30.17   | 2.89 to 33.15     |
| index ranges \(h,k,l\) | -15 ... 15, -12 ... 11, -18 ... 18 | -10 ... 10, -16 ... 16, -10 ... 10 | -8 ... 7, 0 ... 30, 0 ... 11 | -13 ... 13, -19 ... 18, -41 ... 41 | -10 ... 11, -31 ... 30, -12 ... 12 |
| reflections measured | 5720               | 10624            | 61160           | 99187           | 37741             |
| unique \([R_{int}]\) | 2567 [0.0283]      | 1780 [0.0474]    | 2975 [0.0595]   | 5790 [0.0780]   | 4360 [0.0394]     |
| observed \([I\geq2\sigma(I)]\) | 3025              | 1566             | 2658            | 4692            | 3917              |
| data / restraints/parameters | 3025 / 0 / 167 | 1780 / 0 / 102  | 2975 / 0 / 166  | 5790 / 0 / 270  | 4360 / 0 / 169    |
| \(GooF\) on \(F^2\) | 1.045              | 1.042            | 1.036           | 1.060           | 1.049             |
| \(R\) indices \([F\geq4\sigma(F)]\) | \(R(F), wR(F^2)\) | 0.0352, 0.0937   | 0.0396, 0.0982  | 0.0283, 0.0707  | 0.0379, 0.1375    | 0.0289, 0.1375 |
| \(R\) indices (all data) | \(R(F), wR(F^2)\) | 0.0426, 0.0986   | 0.0453, 0.1037  | 0.0333, 0.0742  | 0.0995, 0.0886    | 0.0780, 0.0757 |
| largest residual peaks /e·Å⁻³ | 0.291, -0.352 | 0.292, -0.175   | 0.363, -0.313   | 0.424, -0.339   | 0.471, -0.374     |
4 Experimental details for oxidative coupling of \(N\)-ethylcarbazole to \(N,N'\)-diethyl-3,3'-bicarbazole

![Chemical structures](image)

| entry | A          | B          |
|-------|------------|------------|
| 1(ClO\(_4\))\(_2\) [mg/µmol] | 16.754/22.96 | -          |
| 1(BF\(_4\))\(_2\) [mg/µmol] | -          | 8.618/12.24 |
| \(N\)-ethylcarbazole [mg/µmol] | 4.526/23.18 | 2.382/12.20 |
| HBF\(_4\)-OEt\(_2\) (5% in CH\(_3\)CN) [ml/µmol] | 1/365 | 0.55/200 |
| HMB [mg/µmol] | 0.862/5.31 | -          |
| reaction time (temperature) | 15 min (ice cooling) 45 min (r.t.) | 15 min (ice cooling) 35 min (r.t.) |
| conversion to \(N,N'\)-diethyl-3,3'-bicarbazole [%] | 95 | 94 |
| ratio (GFA/substrate) | 1/1 | 1/1 |

**General protocol**

In a Schlenk flask, a HBF\(_4\)-OEt\(_2\) solution (5% in CH\(_3\)CN; \(c = 0.364 \text{ mol·l}^{-1}\)) was added under ice cooling in an argon atmosphere to the reactants \(1^{2+}\) and \(N\)-ethylcarbazole. The reaction was stirred for 15 min under ice cooling and then allowed to warm up to room temperature.

The reaction was stopped by the addition of an aqueous saturated NaHCO\(_3\) solution. The small amount of CH\(_3\)CN and HBF\(_4\)-OEt\(_2\) was removed under high-vacuum. Then an aqueous diluted solution of NaOH (8%) was added (pH > 9), converting all formed \((1+4H)^{4+}\) to \((1+2H)^{2+}\) (for subsequent transfer into the organic phase). A clear solution was obtained that was extracted several times with CH\(_2\)Cl\(_2\). The combined organic phases were dried over Na\(_2\)SO\(_4\), filtrated and condensed.
$^1$H NMR spectrum (600.13 MHz, 295 K, CD$_2$Cl$_2$) for entry A

$N,N'$-diethyl-3,3'-bicarbazole

$^1$H NMR of $N,N'$-diethyl-3,3'-bicarbazole: (600.13 MHz, 295 K, CD$_2$Cl$_2$): $\delta = 1.47$ (t, $J = 7.2$, 7.2 Hz, 6 H), 4.43 (q, $J = 7.3$, 7.2, 7.2 Hz, 4 H), 7.25 (ddd, $J = 7.8$, 6.5, 1.5 Hz, 2 H), 7.51 - 7.47 (m, 4 H), 7.55 (d, $J = 8.4$, 2 H), 7.87 (dd, $J = 8.4$, 1.8 Hz, 2 H), 8.20 (dd, $J = 7.7$, 0.7 Hz, 2 H), 8.44 (bs, 2 H) ppm.
5 Experimental details for oxidative coupling of 3,3''-dimethoxy-3',4'-dimethyl-o-terphenyl to 3,10-dimethoxy-6,7-dimethyltriphenylene

| entry | A [mg/µmol] | B [mg/µmol] |
|-------|-------------|-------------|
| 1(BF$_4$)$_2$ | 6.562/9.32 | - |
| 1(PF$_6$)$_2$ | - | 7.402/9.02 |
| 3,3''-dimethoxy-3',4'-dimethyl-o-terphenyl [µmol] | 6.25 | 5.7 |
| HBF$_4$·OEt$_2$ (5% in CH$_3$CN) [ml/µmol] | 0.5/182 | 0.5/182 |
| HMB [mg/µmol] | 1.618/9.97 | 0.734/4.52 |
| reaction time (temperature) | 10 min (ice cooling) 120 min (r.t.) | 10 min (ice cooling) 85 min (r.t.) |
| conversion to 3,10-dimethoxy-6,7-dimethyltriphenylene [rel. to applied substrate, %] | 76 | 71 |
| ratio (GFA/substrate) | 1/0.7 | 1/0.6 |

General protocol

In a Schlenk flask, 0.5 ml of a HBF$_4$·OEt$_2$ solution (5% in CH$_3$CN, c = 0.364 mol·l$^{-1}$) was added under ice cooling in an argon atmosphere to the reactants 1$^{2+}$ and to an appropriate volume of a 3,3''-dimethoxy-3',4'-dimethyl-o-terphenyl - solution (c = 0.284 mol·l$^{-1}$ in CH$_3$CN). The reaction was stirred for 10 min under ice cooling and then allowed to warm up to room temperature.

The reaction was stopped by the addition of an aqueous saturated NaHCO$_3$ solution. The small amount of CH$_3$CN and HBF$_4$·OEt$_2$ was removed under high-vacuum. Then an aqueous diluted solution of NaOH (8%) was added (pH > 9), converting all formed (1+4H)$^{4+}$ to (1+2H)$^{2+}$ (for subsequent transfer into the organic phase). A clear solution was obtained that was extracted several times with CH$_2$Cl$_2$. The combined organic phases were dried over Na$_2$SO$_4$, filtrated and condensed.
$^1$H NMR spectrum (399.87 MHz, 294.5 K, CD$_2$Cl$_2$) for entry A

$^1$H NMR of 3,10-dimethoxy-6,7-dimethyltriphenylen: (399.87 MHz, 294.5 K, CD$_2$Cl$_2$):
$\delta = 2.53$ (s, 6 H), 4.00 (s, 6 H), 7.21 (dd, $J = 9.0$, 2.6 Hz, 2 H), 7.99 (d, 2.6 Hz, 2 H), 8.33 (s, 2 H), 8.44 (d, $J = 9.0$ Hz, 2 H) ppm.
Experimental details for reaction of 1(PF₆)₂ with 10-methyl-9,10-dihydroacridine (AcrH₂)

![Chemical structure](image)

| entry | A          | B          | C          |
|-------|------------|------------|------------|
| 1(PF₆)₂ [mg/µmol] | 5.308/6.47 | 5.354/6.52 | 5.312/6.47 |
| AcrH₂ [µmol]       | 6.45       | 6.45       | 6.45       |
| HMB [mg/µmol]      | 0.794/4.89 | 1.05/6.47  | 0.932/5.74 |
| HBF₄·OEt₂ (10% in CD₃CN) [µl/µmol/eq. rel. to 1(PF₆)₂] | 60/44/7    | 90/65/10   | -          |
| CD₃CN [ml]         | 0.45       | 0.45       | 0.45       |
| reaction time (temperature) | 390 min (r.t.) | 250 min (r.t.) | 2 d (60°C) |
| ratio (GFA/substrate) | 1/1         | 1/1        | 1/1        |
| conversion to AcrH⁺ [%] | 90          | 92         | traces     |

General protocol (NMR experiments)

Under an argon atmosphere 0.25 ml of a solution of 10-methyl-9,10-dihydroacridine (c = 0.0258 mol·l⁻¹ in CH₃CN) was transferred in a flame-sealable NMR tube and the solvent was removed under high-vacuum. In a Schlenk flask 1(PF₆)₂ and HMB were dissolved in 0.45 ml CD₃CN and added via syringe to the 10-methyl-9,10-dihydroacridine. HBF₄·OEt₂ (10% in CD₃CN, c = 0.729 mol·l⁻¹) was added via microliter syringe (entry A, B). The NMR tube was flame-sealed in vacuum at -196 °C.
Experimental Details for 10-methyl-9,10-methylacridane (AcrH₂)

This compound was synthesised according to literature procedure\textsuperscript{[1]} using 750 mg (19.7 mmol) LiAlH₄, 375 mg (1.71 mmol) 10-methylacridone and 50 ml diethylether.

Workup\textsuperscript{[2]}: the reaction mixture was quenched by H₂O, extracted several times with ethylacetate and dried over MgSO₄. After the organic layer had been filtered and concentrated the crude product was purified by column chromatography on silica gel (d = 2.5 cm, h = 20 cm, PE (40/60)/toluene = 4/1, Rf: 0.39) to afford 270 mg (1.38 mmol, 81\%) of a white solid. Elemental analysis calcd. (\%) for C₁₄H₁₃N (195.26 g·mol⁻¹): C 86.12, H 6.71, N 7.17; found C 86.04, H 6.94, N 7.24.

\textsuperscript{1}H NMR spectrum (399.89 MHz, 295 K, CD₃CN) for 10-methyl-9,10-dihydroacridine (AcrH₂)

\begin{figure}
\centering
\includegraphics[width=\textwidth]{1H_NMR_AcrH2}
\caption{\textsuperscript{1}H NMR of AcrH₂: (399.89 MHz, 295 K, CD₃CN): δ = 3.35 (s, 3 H), 3.85 (s, 2 H), 6.94 (m, 4 H), 7.18 (m, 4 H) ppm.}
\end{figure}

\begin{thebibliography}{99}
\bibitem{1} P. Karrer, L. Szabo, H. J. Krishna, R. Schwyzzer, \textit{Helv. Chim. Acta} \textbf{1950}, \textit{33}, 294-300.
\bibitem{2} Á. Pintér, A. Sud, D. Sureshkumar, M. Klussmann, \textit{Angew. Chem. Int. Ed.} \textbf{2010}, \textit{49}, 5004-5007.
\end{thebibliography}
$^{13}$C NMR spectrum (100.56 MHz, 295 K, CD$_3$CN) for 10-methyl-9,10-dihydroacridine (AcrH$_2$)

$^{13}$C NMR of AcrH$_2$: (100.56 MHz, 295 K, CD$_3$CN): $\delta = 33.44, 33.60, 112.92, 121.48, 125.15, 127.80, 128.27, 144.62$ ppm.
$^1$H NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry A: first measurement

- HBF$_4$·OEt$_2$
- (1+2H)$^{4+}$
- (1+4H)$^{4+}$
- AcrH$_2$ protonated
- AcrH$^+$
- * impurity of HBF$_4$·OEt$_2$

$^1$H NMR spectrum (600.13 MHz, 295 K, CD$_3$CN) for entry A: last measurement

- HBF$_4$·OEt$_2$
- (1+4H)$^{4+}$
- AcrH$^+$
- * impurity of HBF$_4$·OEt$_2$
7  Experimental details for reaction of 1(PF$_6$)$_2$ with 10-methyl-[9,9'-$^2$H$_2$]-acridine (AcrD$_2$)

![Chemical structure](image)

| entry                  | A [mg/µmol] | B [mg/µmol] |
|------------------------|-------------|-------------|
| 1(PF$_6$)$_2$ [mg/µmol] | 5.364/6.54  | 5.382/6.56  |
| AcrD$_2$ [µmol]        | 6.50        | 6.50        |
| HMB [mg/µmol]          | 0.708/4.36  | 0.622/3.83  |
| HBF$_4$·OEt$_2$ (10% in CD$_3$CN) [µl/µmol/ eq. rel. to 1(PF$_6$)$_2$] | 40/29/4.5 | 90/65/10 |
| CD$_3$CN [ml]          | 0.45        | 0.45        |
| reaction time (temperature) | 630 min (r.t.) | 400 min (r.t.) |
| ratio (GFA/substrate)  | 1/1         | 1/1         |
| conversion to AcrD$^+$ [%] | 87          | 90          |

**General protocol (NMR experiments)**

Under an argon atmosphere 0.25 ml of a solution of 10-methyl-[9,9'-$^2$H$_2$]-10-acridine (c = 0.0260 mol·l$^{-1}$ in CH$_3$CN) was transferred into a flame-sealable NMR tube and the solvent was removed under high-vacuum. In a Schlenk flask 1(PF$_6$)$_2$ and HMB were dissolved in 0.45 ml CD$_3$CN and added via syringe to the [9,9'-$^2$H$_2$]-10-methylacridine. HBF$_4$·OEt$_2$ (10% in CD$_3$CN, c = 0.729 mol·l$^{-1}$) was added via microliter syringe. The NMR tube was flame-sealed in vacuum at -196 °C.
Experimental Details for 10-methyl-[9,9'-2H2]-acridine (AcrD2)

This compound was synthesised according to literature procedure[1] using 255.7 mg (6.1 mmol) LiAlD₄, 116 mg (0.554 mmol) 10-methylacridone and 30 ml diethylether.

Workup[2]: the reaction mixture was quenched by H₂O, extracted several times with ethylacetate and dried over MgSO₄. After the organic layer had been filtered and concentrated the crude product was purified by column chromatography on silica gel (d = 2.5 cm, h = 20 cm, PE (40/60)/toluene 4:1, Rf: 0.33) to afford 62 mg (0.31 mmol, 57%) of a white solid. Elemental analysis calcd. (%) for C₁₄H₁₁ND₂ (197.27 g·mol⁻¹): C 85.24, H 6.64, N 7.10; found C 85.06, H 6.98, N 6.85.

¹H NMR spectrum (399.89 MHz, 295.2 K, CD₃CN) for 10-methyl-[9,9'-2H2]-acridine (AcrD2)

¹H NMR of AcrD₂: (399.87 MHz, 295.2 K, CD₃CN): δ = 3.35 (s, 3 H), 6.94 (m, 4 H), 7.18 (m, 4 H) ppm. 

[1] P. Karrer, L. Szabo, H. J. Krishna, R. Schwzyzer, Helv. Chim. Acta 1950, 33, 294-300.
[2] Á. Pintér, A. Sud, D. Sureshkumar, M. Klussmann, Angew. Chem. Int. Ed. 2010, 49, 50–04–5007.
\(^{13}\)C NMR spectrum (100.56 MHz, 295.2 K, CD\(_3\)CN) for 10-methyl-[9,9\(^{-2}\)H\(_2\)]-acridine (AcrD\(_2\))

\(^{13}\)C NMR of AcrD\(_2\): (100.56 MHz, 295.3 K, CD\(_3\)CN): \(\delta = 33.60, 112.91, 121.47, 125.04, 127.80, 128.28, 144.62 \) ppm.

\(^2\)D NMR spectrum (92.12 MHz, 295 K, CH\(_3\)CN) for 10-methyl-[9,9\(^{-2}\)H\(_2\)]-acridine (AcrD\(_2\))
\(^1\)H NMR spectrum (199.87 MHz, 298 K, CD\(_3\)CN) for entry A: first measurement

- HBF\(_4\)·OEt\(_2\)
- (1+2H)\(^+\)
- (1+4H)\(^+\)
- AcrD\(_2\) protonated
- AcrD\(^+\)
- * impurities of HBF\(_4\)·OEt\(_2\)

\(^1\)H NMR spectrum (399.89 MHz, 295.2 K, CD\(_3\)CN) for entry A: last measurement

- HBF\(_4\)·OEt\(_2\)
- (14H)\(^+\)
- AcrD\(^+\)
- * impurities of HBF\(_4\)·OEt\(_2\)
Dependence of the conversion vs. time plots for the reaction between 1(PF$_6$)$_2$ and AcrD$_2$ on the applied equivalents of HBF$_4$·OEt$_2$

![Conversion vs. time plots for 1(PF$_6$)$_2$ and AcrD$_2$](image)

Comparison between the conversion vs. time plots for AcrH$_2$ and AcrD$_2$ in the presence of 10 eq. of HBF$_4$·OEt$_2$

![Conversion vs. time plots for AcrH$_2$ and AcrD$_2$](image)

$^1$H NMR Data (CD$_3$CN)

| AcrH$_2$[a]                      | AcrD$_2$[b]                      | AcrH$^+$_[c]                      | AcrD$^+$_[a]                      |
|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| 7.18 (m, 4 H), 6.94 (m, 4 H), 3.85 (s, 2 H), 3.35 (s, 3 H) | 7.18 (m, 4 H), 6.94 (m, 4 H), 3.35 (s, 3 H) | 9.86 (s, 1 H), 8.53 (m, 4 H), 8.41 (t, 2 H), 7.99 (t, 2 H), 4.76 (s, 3 H) | 8.56 (t, 4 H), 8.42 (t, 2 H), 7.99 (t, 2 H), 4.76 (s, 3 H) |

[a] 399.89 MHz; [b] 199.87 MHz; [c] 600.13 MHz
8 Experimental details for reaction of $1^{2+}$ with 9,10-dihydroanthracene (AnH$_2$)

![Diagram of reaction]

| entry                                                                 | A          | B          | C          |
|-----------------------------------------------------------------------|------------|------------|------------|
| $1$(PF$_6$)$_2$ [mg/µmol]                                             | 8.248/10.05 | -          | 6.838/8.33 |
| $1$(ClO$_4$)$_2$ [mg/µmol]                                           | -          | 5.848/8.01 | -          |
| AnH$_2$ [mg/µmol]                                                     | 2.048/11.36 | 1.442/8.00 | 1.514/8.40 |
| HBF$_4$·OEt$_2$ (10% in CD$_3$CN) [µL/µmol/eq. rel. to $1^{2+}$]     | 69/50/5    | 88/64/8    | 103/75/9   |
| HMB [mg/µmol]                                                        | 0.938/5.78 | 1.184/7.30 | 0.776/4.78 |
| CD$_3$CN [ml]                                                         | 0.45       | 0.45       | 0.45       |
| reaction time (temperature)                                          | 180 min (r.t.) | 60 min (r.t.) | 90 min (r.t.) |
| ratio (GFA/substrate)                                                 | 1/1.1      | 1/1        | 1/1        |
| conversion to anthracene (An) [%]                                    | 78$^a$     | 62         | 65         |

$^a$ rel. to $(1+4H)^{4+}$

**General protocol (NMR experiments)**

In a Schlenk flask $1^{2+}$, HMB and 9,10-dihydroanthracene were dissolved in 0.45 ml CD$_3$CN and transferred via syringe into a flame-sealable NMR tube. HBF$_4$·OEt$_2$ (10% in CD$_3$CN, c = 0.729 mol·l$^{-1}$) was added via microliter syringe. The NMR tube was flame-sealed in vacuum at -196 °C.
$^1$H NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry A: first measurement

$^1$H NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry A: measurement after 2 h
\(^1\)H NMR spectrum (600.13 MHz, 295 K, CD\(_3\)CN) for entry A: last measurement

\[
\begin{align*}
&\text{(1+4H)}^{4+} \\
&\text{AnH}_2 \\
&\text{An} \\
&\text{HBF}_4 \cdot \text{OEt}_2 \\
\ast &\text{impurity of HBF}_4 \cdot \text{OEt}_2
\end{align*}
\]

Plot showing the conversion as a function of time for the reaction between 1(PF\(_6\))\(_2\) and 9,10-dihydroanthracene in the presence of 5 eq. and 9 eq. HBF\(_4\)·OEt\(_2\)

Please note that the conversion in this plot refers to the decay of the dihydroanthracene (AnH\(_2\)) signals in the \(^1\)H NMR spectrum. By contrast, the conversion to anthracene (NMR yield) given in the tables are determined from the anthracene (An) signal integrals relative to the guanidine signal integrals. The different procedures are necessary due to the formation of the radical AnH\(^+\) as reaction intermediate, leading to temporary broad product signals not applicable for integration in the course of the reaction.
9 Experimental details for reaction of 1(PF₆)₂ with 1-benzyl-1,4-dihydrronicotinamide (BNAH)

![Chemical structure]

| entry                                      | A          | B          |
|--------------------------------------------|------------|------------|
| 1(PF₆)₂ [mg/µmol]                          | 5.314/6.48 | 4.024/4.90 |
| BNAH [mg/µmol]                             | 1.440/6.72 | 1.042/4.86 |
| HMB [mg/µmol]                              | 0.822/5.07 | 0.660/4.07 |
| CD₃CN [ml]                                 | 0.45       | 0.45       |
| reaction time (temperature)                | 24 h (60 °C) | 24 h (40 °C) |
| ratio (GFA/substrate)                       | 1/1        | 1/1        |
| conversion to BNAH⁺ [rel. to 1²⁺/(1+nH)ⁿ⁺, %] | 27         | 24         |

General protocol (NMR experiments)

In a Schlenk flask 1(PF₆)₂, HMB and BNAH were dissolved in 0.45 ml CD₃CN and transferred via syringe into a flame-sealable NMR tube. The NMR tube was flame-sealed in vacuum at -196 °C. The tube was heated to 60 °C or in case of entry B to 40 °C.
$^1$H NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry A: first measurement

$^{12+}$
BNAH

$^1$H NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry A: measurement after 24 h

$(1+nH)^n$ $^{12+}$
BNAH
BNAH$^+$
Prolonged reaction times (2 d) lead to complete consumption of $1^{2+}$, but also to degradation of BNAH$^+$. 

$^1$H NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry A: measurement after 2d
10 Experimental details for the PCET reaction between $2\text{(PF}_6\text{)}_2$ and $(1+2\text{H})(\text{PF}_6\text{)}_2$

![Chemical structures](image)

**UV-vis experiments**

Three solutions were prepared (solution I – III, see Table below). Under argon atmosphere a 1 cm quartz glass cuvette was filled with 3.0 ml of solution I. Under stirring 9.3 µl of solution II was added. For the reaction in entry B, 3.8 µl of solution III was also added. The conversion was followed by UV-vis spectroscopy.

|               | solution I   | solution II  | solution III  |
|---------------|--------------|--------------|--------------|
| [mg/mmol]     | $2\text{(PF}_6\text{)}_2$ | $(1+2\text{H})(\text{PF}_6\text{)}_2$ | HBF$_4$·OEt$_2$ |
| CH$_3$CN [ml] | 25           | 5            | 2            |
| c [mol·l$^{-1}$] | $1.87\cdot10^{-5}$ | $6.05\cdot10^{-3}$ | $3.67\cdot10^{-3}$ |

| entry | A | B |
|-------|---|---|
| solution I [ml/mmol] | $3/5.61\cdot10^{-5}$ | $3/5.61\cdot10^{-5}$ |
| solution II [µl/mmol] | $9.3/5.62\cdot10^{-5}$ | $9.3/5.62\cdot10^{-5}$ |
| solution III [µl/mmol] | | $3.8/1.4\cdot10^{-5}$ |
| ratio $2^{2+}/(1+2\text{H})^{2+}$ | 1/1 | 1/1 |
| ratio $2^{2+}$/HBF$_4$·OEt$_2$ | | 1/0.25 |
UV-vis spectra for entry A
(without HBF$_4$·OEt$_2$)

UV-vis spectra for entry B
(with HBF$_4$·OEt$_2$)
Plot of the absorptions at 420 nm (band of the product $1^{2+}$) and 325 nm (dominating contribution from the reactant $2^{2+}$) in dependence of the reaction time.
NMR experiments for the reaction of 2(PF₆)₂ with (1+2H)(PF₆)₂

Protocol: The two reactants, 5.94 mg (0.01 mmol) of 2(PF₆)₂ and 8.22 mg (0.01 mmol) of (1+2H)(PF₆) were weighed into an NMR tube and dissolved in 8 ml CD₃CN (c = 1.25·10⁻² mol·l⁻¹). The reaction was followed by ¹H NMR spectroscopy. Already the first measurements showed quantitative conversion.

¹H NMR spectrum (199.87 MHz, 298 K, CD₃CN) for the reaction between 2(PF₆)₂ and (1+2H)(PF₆)₂: first measurement after 5 min at 298 K
Experiments with different concentrations of HBF₄·OEt₂

After completion of the reaction, 3-5 μl portions of a solution of HBF₄·OEt₂ (0.12 g·ml⁻¹ in CD₃CN, c = 7.3·10⁻¹ mol·l⁻¹) were added. The ratio 2²⁺/ HBF₄·OEt₂ was estimated by NMR spectroscopy. An excess of HBF₄·OEt₂ leads to formation of the twofold-protonated, oxidized compound (1+2H)⁴⁺, but not to PCET.

¹H NMR spectra (199.87 MHz, 298 K, CD₃CN)
**Stopped flow UV-vis measurements:**

First, stock solutions of (1+2H)(PF$_6$)$_2$ (solution I) and 2(PF$_6$)$_2$ (solution II) were prepared. By stepwise dilution of solution II, three further solutions (III-V) of 2(PF$_6$)$_2$ with decreasing concentrations were obtained.

|                  | solution I          | solution II         |
|------------------|---------------------|---------------------|
|                  | (1+2H)(PF$_6$)$_2$  | 2(PF$_6$)$_2$       |
| [mg/mmol]        | 0.660/8.02·10$^{-4}$| 18.698/3.15·10$^{-2}$|
| CH$_3$CN [ml]    | 10                  | 10                  |
| c [mol·l$^{-1}$] | 8.02·10$^{-5}$      | 3.15·10$^{-3}$      |

Solution I

|                  | solution III | solution IV | solution V |
|------------------|--------------|-------------|------------|
|                  | solution II [5] | solution III [5] | solution IV [1] |
| CH$_3$CN [ml]    | 5            | 5           | 9          |
| c [mol·l$^{-1}$] | 1.57·10$^{-3}$ | 7.87·10$^{-4}$ | 7.87·10$^{-5}$ |

Then the two storage vessels of the instrument were charged with solution I and one of the solutions II-V, and the measuring cell filled with equal volumes of both solutions. The following concentrations and molar ratios between the two reactants result.

| entry          | A                  | B                  | C                  | D                  |
|----------------|--------------------|--------------------|--------------------|--------------------|
| solution / c [mol·l$^{-1}$] | II/1.57·10$^{-3}$ | III/7.87·10$^{-4}$ | IV/3.93·10$^{-4}$ | V/3.93·10$^{-5}$ |
| solution I c [mol·l$^{-1}$] | 4.01·10$^{-5}$     | 4.01·10$^{-5}$     | 4.01·10$^{-5}$     | 4.01·10$^{-5}$     |
| ratio          | 1 : 39             | 1 : 19.6           | 1 : 9.8            | 1 : 0.98           |
First order plots of the absorption at 420 nm in dependence of the reaction time for the initial stage of the reaction between \((1+2H)(PF_6)_2\) and an excess of \(2(PF_6)_2\). The pseudo-first order rate constants \(k_{obs}\) result from linear fits.

\[
\begin{align*}
\text{entry A} & : & k_{obs} &= (0.374 \pm 0.083) \text{ s}^{-1} \\
\text{entry B} & : & k_{obs} &= (0.264 \pm 0.041) \text{ s}^{-1} \\
\text{entry C} & : & k_{obs} &= (0.111 \pm 0.017) \text{ s}^{-1}
\end{align*}
\]

Plot of the \(k_{obs}\) values as a function of the concentration of \(2^{2+}\) in the solution. From a linear fit the second order rate constant is estimated to be \(k_H = 257 \pm 27 \text{ M}^{-1}\text{s}^{-1}\) at room temperature.
11 Experimental details for reaction of $2(\text{PF}_6)_2$ with 1-benzyl-1,4-dihydronicotinamide (BNAH)

![Chemical structures]

| entry                          | A            |
|--------------------------------|--------------|
| $2(\text{PF}_6)_2$ [mg/µmol]   | 3.924/6.60   |
| BNAH [mg/µmol]                 | 1.42/6.63    |
| HMB [mg/µmol]                  | 0.856/5.28   |
| CD$_3$CN [ml]                  | 0.45         |
| reaction time (temperature)    | < 1 min (r.t.)|
| ratio (GFA/substrate)           | 1/1          |
| conversion to BNAH$^+$ [%]      | >99          |

**General protocol (NMR experiments)**

In a Schlenk flask $2(\text{PF}_6)_2$, HMB and BNAH were dissolved in 0.45 ml CD$_3$CN and transferred via syringe into a flame-sealable NMR tube. The NMR tube was flame-sealed in vacuum at -196 °C.
$^1$H NMR spectrum (600.13 MHz, 294.9 K, CD$_3$CN) for entry A

(2+nH)$^{n+}$

BNAH$^+$

$^1$H NMR of BNAH$: (600.13$ MHz, 294.9 K, CD$_3$CN): $\delta = 5.76$ (s, 2 H), 7.49 (m, 5 H), 8.10 (dd, $J = 7.69, 6.52$ Hz, 1 H), 8.79 (dd, 15.99, 7.13 Hz, 2 H), 9.15 (s, 1 H) ppm.
12 Experimental details for reaction of $2(PF_6)_2$ with 10-methyl-9,10-dihydroacridine ($AcrH_2$)

![Chemical structure](image)

| entry | A               | B               | C               |
|-------|-----------------|-----------------|-----------------|
| $2(PF_6)_2$ [mg/µmol] | 7.76/13.06      | 3.912/6.58      | 3.568/6.00      |
| $AcrH_2$ [µmol]       | 6.45            | 6.45            | 6.45            |
| HMB [mg/µmol]         | 0.598/3.69      | 1.06/6.53       | 0.914/5.63      |
| CD$_3$CN [ml]         | 0.45            | 0.45            | 0.45            |
| reaction time (temperature) | 160 min (r.t.) | 180 min (r.t.) | 180 min (r.t.) |
| ratio (GFA/substrate) | 1/0.5           | 1/1             | 1/1.1           |
| conversion to $AcrH^+$ [%] | 92$^b$         | 73              | 74$^a$          |

$^a$ rel. to $(2+nH)^{n+}$

$^b$ rel. to applied $AcrH_2$

**General protocol (NMR experiments)**

Under an argon atmosphere 0.25 ml of a solution of 10-methyl-9,10-dihydroacridine ($c = 0.0258$ mol·l$^{-1}$ in CH$_3$CN) was transferred into a flame-sealable NMR tube and the solvent was removed under high-vacuum. In a Schlenk flask $2(PF_6)_2$ and HMB were dissolved in 0.45 ml CD$_3$CN and added via syringe to the 10-methyl-9,10-dihydroacridine. The NMR tube was flame-sealed in vacuum at -196 °C.
$^1$H NMR spectrum (200.13 MHz, 298 K, CD$_3$CN) for entry A: first measurement

$^{2+}$
$(2+n\text{H})^{n+}$
AcrH$_2$
AcrH$^+$

$^1$H NMR spectrum (200.13 MHz, 298 K, CD$_3$CN) for entry A: last measurement

$^{2+}$
$(2+n\text{H})^{n+}$
AcrH$_2$
AcrH$^+$
* by-products and AcrH$_2$
The NMR spectrum recorded after 180 min still shows the presence of AcrH$_2$. Hence one might expect higher conversion for longer reaction times. However, prolonged reaction times led to the appearance of signals due to unidentified by-products, without further AcrH$_2$ conversion.
13 Experimental details for reaction of $2 \text{(PF}_6\text{)}_2$ with 10-methyl-[9,9'-$^2\text{H}_2$]-acridine (AcrD$_2$)

![Chemical structures]

| entry | A                  | B                  |
|-------|--------------------|--------------------|
| $2 \text{(PF}_6\text{)}_2$ [mg/µmol] | 6.862/11.55        | 3.168/5.33         |
| AcrD$_2$ [µmol]                     | 6.50               | 6.50               |
| HMB [mg/µmol]                       | 0.436/2.69         | 0.708/4.36         |
| CD$_3$CN [ml]                       | 0.45               | 0.45               |
| reaction time (temperature)         | 460 min (r.t.)     | 400 min (r.t.)     |
| ratio (GFA/substrate)               | 1/0.6              | 1/1.2              |
| conversion to AcrD$^+$ [%]           | 80$^b$             | 59$^a$             |

$^a$ rel. to $(2+nD)^{n+}$  
$^b$ rel. to applied AcrD$_2$

**General protocol (NMR experiments)**

Under an argon atmosphere 0.25 ml of a solution of 10-methyl-[9,9'-$^2\text{H}_2$]-acridine ($c = 0.026$ mol·l$^{-1}$ in CH$_3$CN) was transferred into a flame-sealable NMR tube and the solvent was removed under high-vacuum. In a Schlenk flask $2 \text{(PF}_6\text{)}_2$ and HMB were dissolved in 0.45 ml CD$_3$CN and added via syringe to the 10-methyl-[9,9'-$^2\text{H}_2$]-acridine. The NMR tube was flame-sealed in vacuum at -196 °C.
$^1$H NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry A: first measurement

2$^{2+}$
$(2+nD)^{n+}$
AcrD$_2$
AcrD$^+$

$^1$H NMR spectrum (399.89 MHz, 295.3 K, CD$_3$CN) for entry A: last measurement

2$^{2+}$
$(2+nD)^{n+}$
AcrD$_2$
AcrD$^+$
* by-products + AcrD$_2$
$^{1}H$ NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry B: last measurement
14 Experimental details for reaction of 2(PF$_6$)$_2$ with 9,10-dihydroanthracene (AnH$_2$)

![Chemical structure of reactants and products]

| entry | A                  | B                  |
|-------|--------------------|--------------------|
| 2(PF$_6$)$_2$ [mg/µmol] | 5.052/8.50         | 4.676/7.87         |
| AnH$_2$ [mg/µmol]      | 1.994/11.06        | 1.550/8.60         |
| NH$_4$PF$_6$ [mg/µmol]  | -                  | 2.5/15.34          |
| HMB [mg/µmol]          | 0.808/4.98         | 1.006/6.20         |
| CD$_3$CN [ml]          | 0.45               | 0.45               |
| reaction time (temperature) | 50 h (60 °C)       | 50 h (60 °C)       |
| ratio (GFA/substrate)   | 1/1.3              | 1/1.1              |
| conversion to anthracene (An) [rel. to (2+2H)$_2^2+$/2$^2+$, %] | 6                  | 29                 |

**General protocol (NMR experiments)**

In a Schlenk flask 2(PF$_6$)$_2$, HMB and 9,10-dihydroanthracene (and NH$_4$PF$_6$ for entry B) were dissolved in 0.45 ml CD$_3$CN and transferred via syringe into a flame-sealable NMR tube. The NMR tube was flame-sealed in vacuum at -196 °C.
\(^1\)H NMR spectrum (199.87 MHz, 298 K, CD\(_3\)CN) for entry A: first measurement

\(^1\)H NMR spectrum (199.87 MHz, 298 K, CD\(_3\)CN) for entry A: last measurement

\(^1\)H NMR of anthracene: (199.87 MHz, 298 K, CD\(_3\)CN): \(\delta = 7.51\) (dd, \(J = 6.6, 3.2\) Hz, 4 H), 8.06 (dd, \(J = 6.3, 3.9\) Hz, 4 H), 8.52 (s, 2 H) ppm.
$^1$H NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry B: first measurement

$^1$H NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry B: last measurement
Conversion vs. time plot for the reaction between $2(\text{PF}_6)_2$ and 9,10-dihydroanthracene ($\text{AnH}_2$)
Experimental details for reaction of $2(PF_6)_2$ with 3,3''',4,4'''-tetramethoxy-α-terphenyl (TMTP) to 2,3,10,11-tetramethoxy-triphenylene

![Chemical structures]

a) Without HBF$_4$·OEt$_2$

| entry                        | A                  |
|------------------------------|--------------------|
| $2(PF_6)_2$ [mg/µmol]        | 3.108/5.23         |
| 3,3''',4,4'''-tetramethoxy-α-terphenyl [mg/µmol] | 1.824/5.21 |
| CD$_3$CN [ml]                | 0.5                |
| reaction time (temperature)  | 60 min (333 K)     |
| ratio (GFA/substrate)        | 1/1                |
| conversion to 2,3,10,11-tetramethoxy-triphenylene [%] | 0.01 |

General protocol (NMR experiments)

In an NMR tube, the two reactants $2(PF_6)_2$ and 3,3''',4,4'''-tetramethoxy-α-terphenyl were dissolved in CD$_3$CN. After addition of HBF$_4$·OEt$_2$ (0.12 g·ml$^{-1}$ in CD$_3$CN), conversion was followed by $^1$H NMR spectroscopy.
$^1$H NMR spectrum for entry A (199.87 MHz, 298 K, CD$_3$CN) for 2(PF$_6$)$_2$ + 3,3''',4,4'''-tetramethoxy-o-terphenyl in the absence of HBF$_4$·OEt$_2$, after 60 min, 333 K
b) With HBF₄·OEt₂

**Experiments at different temperatures**

|                              | B                        | C                        |
|------------------------------|--------------------------|--------------------------|
| 2(PF₆)₂ [mg/µmol]            | 3.422/5.75               | 3.336/5.62               |
| 3,3''',4,4'''-tetramethoxy-o-terphenyl [mg/µmol] | 2.044/5.72               | 1.988/5.67               |
| c [2(PF₆)₂] [mol·l⁻¹]       | 1.14·10⁻²                | 1.04·10⁻²                |
| CD₃CN [ml]                   | 0.5                      | 0.5                      |
| ratio (GFA/substrate)        | 1/1                      | 1/1                      |
| HBF₄·OEt₂ (0.12 g·ml⁻¹ in CD₃CN) [µl/µmol/eq. rel. to 2²⁺] | 1.0/0.73/0.13            | 10/7.35/1.3              |
| Reaction time (temperature) | 300 min (298 K)          | 10 min (333 K)           |
| conversion to 2,3,10,11-tetramethoxy-triphenylene after workup [%] | 88                      | 96                       |

**Workup:**

The reaction was stopped by the addition of an aqueous saturated NaHCO₃ solution. The small amount of CD₃CN was removed under high-vacuum. Then an aqueous diluted solution of NaOH (8%) was added (pH > 9), (converting all formed (2+2H)²⁺ to 2) A clear solution was obtained that was extracted several times with CH₂Cl₂. The combined organic phases were dried over Na₂SO₄, filtrated and condensed.
Please note that the conversion in this plot is determined from the integration of $^1$H NMR signals of $2^{2+}$ and $(2+2H)^{2+}$. By contrast, the conversion (NMR yield) given in the table was determined after workup. This procedure is necessary due to the emergence of radical intermediates.
$^1$H NMR spectrum for entry B (199.87 MHz, 298 K, CD$_2$Cl$_2$) after workup

$^1$H NMR spectrum for entry C (199.87 MHz, 298 K, CD$_2$Cl$_2$) after workup
Experimental details for reaction of $2{(PF_6)}_2$ with $p$-dihydro-benzoquinone to $p$-benzoquinone

NMR experiments at different concentrations (keeping the 1:1 molar ratio of both reactants)

Protocol: First, two stock solutions were prepared. Stock solution I: 31.774 mg (0.0535 mmol) of $2{(PF_6)}_2$ in 0.85 ml CD$_3$CN ($c = 6.26 \cdot 10^{-2} \text{ mol·l}^{-1}$); stock solution II: 5.932 mg (0.0538 mmol) $p$-dihydro-benzoquinone in 0.86 ml CD$_3$CN ($c = 6.26 \cdot 10^{-2} \text{ mol·l}^{-1}$). Equimolar mixtures were then prepared, in which the concentration of both reactants varied (while keeping a 1:1 molar ratio between them).

| entry                        | A   | B   | C   | D   |
|------------------------------|-----|-----|-----|-----|
| solution I [ml]              | 0.25| 0.18| 0.1 | 0.05|
| $2{(PF_6)}_2$ [µmol]         | 15.7| 11.3| 6.26| 3.13|
| solution II [ml]             | 0.25| 0.18| 0.1 | 0.05|
| $p$-dihydro-benzoquinone [µmol] | 15.7| 11.3| 6.26| 3.13|
| ratio $2^{2+}$/$p$-dihydro-benzoquinone | 1/1 | 1/1 | 1/1 | 1/1 |
| CD$_3$CN [ml]                | 0   | 0.14| 4.8 | 4.9 |
| $c$ [mol·l$^{-1}$]           | $3.13 \cdot 10^{-2}$ | $2.25 \cdot 10^{-2}$ | $1.25 \cdot 10^{-2}$ | $1.0 \cdot 10^{-2}$ |
| reaction time (temperature)  | 60 min (298 K) | 60 min (298 K) | 30 min (298 K) | 15 min (298 K) |
| conversion [%]               | 99  | 99  | 99  | 99  |
$^1$H NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry D: first measurement after 2.5 min, 298 K

$2^{2+}$
$(2+2H)^{2+}$
$p$-dihydro-benzoquinone
$p$-benzoquinone

chemical shift (ppm)
\(^1\)H NMR spectrum (199.87 MHz, 298 K, CD\textsubscript{3}CN) for entry D: last measurement after 60 min, 298 K

NMR experiments at different temperatures

Protocol: Two stock solutions were prepared. Stock solution I: 22.46 mg (0.038 mmol) of \(2\)(PF\textsubscript{6})\textsubscript{2} in 1.3 ml CD\textsubscript{3}CN (c = 2.9\cdot10^{-2} \text{ mol}\cdot\text{l}^{-1}); stock solution II: 4.038 mg (0.037 mmol) \(p\)-dihydro-benzoquinone in 1.26 ml CD\textsubscript{3}CN (c = 2.9\cdot10^{-2} \text{ mol}\cdot\text{l}^{-1}). Then equimolar mixtures of the two solutions were prepared and the conversion followed by \(^1\)H NMR spectroscopy at different reaction temperatures.

| entry       | solution I [ml] | E   | F   | G   | H   |
|-------------|-----------------|-----|-----|-----|-----|
|             | \(2\)(PF\textsubscript{6})\textsubscript{2} [\mu mol] | 7.3 | 7.3 | 7.3 | 7.3 |
| solution II | [ml]            | 0.25| 0.25| 0.25| 0.25|
|             | \(p\)-dihydro-benzoquinone [\mu mol] | 7.3 | 7.3 | 7.3 | 7.3 |
|             | ratio \(2^{2+}/p\)-dihydro-benzoquinone | 1/1 | 1/1 | 1/1 | 1/1 |
|             | reaction time (temperature) | 60 min (298 K) | 50 min (308 K) | 25 min (318 K) | 11.5 min (328 K) |
|             | conversion [%]   | 98  | 99  | >99 | >99 |
$^1\text{H NMR spectrum (199.87 MHz, 298 K, CD}_3\text{CN) for entry E: first measurement after 2.5 min, 298 K}$

$^2\text{H}^2^+\,$
$\text{(2+2H)}^2^+\,$
$\text{p-dihydro-benzoquinone}\,$
$\text{p-benzoquinone}\,$

$^1\text{H NMR spectrum (199.87 MHz, 298 K, CD}_3\text{CN) for entry E: last measurement after 60 min, 298 K}$

$^2\text{H}^2^+\,$
$\text{(2+2H)}^2^+\,$
$\text{p-dihydro-benzoquinone}\,$
$\text{p-benzoquinone}\,$
Plot showing the decrease of $2^{2+}$ (%) with time for different temperatures
17 Reaction of 2(PF<sub>6</sub>)<sub>2</sub> with AcrH<sub>2</sub>

**UV-vis Experiments**

**stock solution I:** 1.386 mg 2(PF<sub>6</sub>)<sub>2</sub> in 25 ml CH<sub>3</sub>CN (c = 9.33·10<sup>-5</sup> mol·l<sup>-1</sup>)

**stock solution II:** 25.2 mg 10-methyl-9,10-dihydroacridine in 5 ml CH<sub>3</sub>CN (c = 0.0258 mol·l<sup>-1</sup>)

Under an argon atmosphere a 1 cm quartz cuvette equipped with a rubber septum was filled with 2.8 ml of stock solution I and with CH<sub>3</sub>CN if noted below. Stock solution II was added quickly with a syringe. The concentration refers to the concentration in the cuvette (3.2 ml). To check the reproducibility, all experiments are repeated and in all cases similar results are obtained.

| entry | stock solution I vol [ml] | stock solution II vol [ml] | CH<sub>3</sub>CN vol [ml] | c [2(PF<sub>6</sub>)<sub>2</sub>] [mol·l<sup>-1</sup>] | c [AcrH<sub>2</sub>] [mol·l<sup>-1</sup>] | eq. |
|-------|---------------------------|---------------------------|---------------------------|---------------------------------|---------------------------------|-----|
| A     | 2.8                       | 0.1                       | 0.3                       | 8.16·10<sup>-5</sup>           | 8.07·10<sup>-4</sup>           | 9.9 |
| B     | 2.8                       | 0.2                       | 0.2                       | 8.16·10<sup>-5</sup>           | 1.61·10<sup>-3</sup>           | 19.7|
| C     | 2.8                       | 0.4                       | -                         | 8.16·10<sup>-5</sup>           | 3.23·10<sup>-3</sup>           | 39.6|

**UV-vis spectra for entry A:**

![UV-vis spectra](image)
Plots of the absorbance at 357 and 420 nm (maxima of the bands due to AcrH+ and 575 nm (reaction intermediate identified as 2+) as a function of reaction time.
UV-vis spectra for entry B:

UV-vis spectra for entry C:

Please note that the bands of AcrH⁺ are less intense as expected based on the known extinction coefficient $\varepsilon_{\text{max}}^{[1]} = 1.8 \cdot 10^4$ M⁻¹·cm⁻¹ for the band at 358 nm.

[1] S. Fukuzumi, K. Okamoto, Y. Tokuda, C. P. Gros, R. Guilard, J. Am. Chem. Soc. 2004, 126, 17059-17066.
18 Reaction of $2(\text{PF}_6)_2$ with $\text{AcrD}_2$

**UV-vis Experiments**

**stock solution I:** 1.428 mg $2(\text{PF}_6)_2$ in 25 ml CH$_3$CN ($c = 9.61 \cdot 10^{-5}$ mol·l$^{-1}$)

**stock solution II:** 25.6 mg 10-methyl-[9, 9'-$^2$H$_2$]-acridine in 5 ml CH$_3$CN ($c = 0.0260$ mol·l$^{-1}$)

Under an argon atmosphere a 1 cm quartz cuvette equipped with a rubber septum was filled with 2.7 ml of stock solution I and CH$_3$CN. Stock solution II was added quickly with a syringe. The concentration refers to the concentration in the cuvette (3.2 ml). To check the reproducibility, all experiments are repeated and in all cases similar results are obtained.

| entry | stock solution I vol [ml] | stock solution II vol [ml] | CH$_3$CN vol [ml] | c [$2(\text{PF}_6)_2$] [mol·l$^{-1}$] | c [AcrH$_2$] [mol·l$^{-1}$] | eq. |
|-------|--------------------------|---------------------------|-------------------|-------------------------------------|----------------------------|-----|
| A     | 2.7                      | 0.1                       | 0.4               | 8.11$\cdot10^{-5}$                  | 8.11$\cdot10^{-4}$         | 10.0 |
| B     | 2.7                      | 0.2                       | 0.3               | 8.11$\cdot10^{-5}$                  | 1.62$\cdot10^{-3}$         | 20.0 |
| C     | 2.7                      | 0.4                       | 0.1               | 8.11$\cdot10^{-5}$                  | 3.24$\cdot10^{-3}$         | 40.0 |

**UV-vis spectra for entry A:**

![UV-vis spectra](image-url)
UV-vis spectra for entry B:

UV-vis spectra for entry C:

Please note that the bands of AcrH⁺ are less intense as expected based on the known extinction coefficient $\varepsilon_{\text{max}}^{[1]} = 1.8 \cdot 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ for the band at 358 nm.

[1] S. Fukuzumi, K. Okamoto, Y. Tokuda, C. P. Gros, R. Guilard, J. Am. Chem. Soc. 2004, 126, 17059-17066.
Experimental details for the PCET reaction between $2(\text{PF}_6)_2$ and $(3+2\text{H})(\text{PF}_6)_2$

**Protocol**

First two stock solutions were prepared. Stock solution I: 29.39 mg (0.05 mmol) $2(\text{PF}_6)_2$ in 1.5 ml CD$_3$CN ($c = 3.33 \cdot 10^{-2}$ mol·l$^{-1}$); stock solution II: 29.45 mg (0.05 mmol) $(3+2\text{H})(\text{PF}_6)_2$ in 1.5 ml CD$_3$CN ($c = 3.33 \cdot 10^{-2}$ mol·l$^{-1}$). Then 0.3 ml of solution I and 0.3 ml of solution II were mixed in an NMR tube and the reaction between $2(\text{PF}_6)_2$ and $(3+2\text{H})(\text{PF}_6)_2$ followed at different temperatures by $^1\text{H}$ NMR spectroscopy.

| entry              | A          | B          | C          | D          |
|--------------------|------------|------------|------------|------------|
| solution I [ml]    | 0.30       | 0.30       | 0.30       | 0.30       |
| $2(\text{PF}_6)_2$ [µmol] | 10         | 10         | 10         | 10         |
| solution II [ml]   | 0.30       | 0.30       | 0.30       | 0.30       |
| $(3+2\text{H})(\text{PF}_6)_2$ [µmol] | 10         | 10         | 10         | 10         |
| ratio $2^{2+}/(3+2\text{H})^{2+}$ | 1/1        | 1/1        | 1/1        | 1/1        |
| reaction time (temperature) | 180 min (298 K) | 95 min (308 K) | 60 min (318 K) | 45 min (328 K) |
| ratio $(3+2\text{H})^{2+}/3^{2+}$ | 0.08/1     | 0.06/1     | 0.075/1    | 0.014/1    |
| conversion to $3(\text{PF}_6)_2$ [%] | 92.6       | 94.3       | 93.0       | 98.6       |
$^1$H NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry B: first measurement after 2.5 min, 308 K

$^1$H NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry B: last measurement after 90 min, 308 K
Conversion vs. time plots for four different temperatures

Analysis on the assumption of a second-order rate law:
Gleichung: $y = a + b \cdot x$

Zeichnen: 

Gewichtung: Keine Gewichtung

Schnittpunkt mit der Y-Achse: $0,00992 \pm 1,31587 \cdot 10^{-4}$

Steigung: $6,71672 \cdot 10^{-6} \pm 3,47632 \cdot 10^{-7}$

Summe der Fehlerquadrate: $9,65818 \cdot 10^{-8}$

Pearson R: 0,99601

R-Quadrat (COD): 0,99203

Kor. R-Quadrat: 0,98937


Gleichung: $y = a + b \cdot x$

Zeichnen: 

Gewichtung: Keine Gewichtung

Schnittpunkt mit der Y-Achse: $0,00976 \pm 1,54793 \cdot 10^{-4}$

Steigung: $1,07467 \cdot 10^{-5} \pm 4,61873 \cdot 10^{-7}$

Summe der Fehlerquadrate: $1,36393 \cdot 10^{-7}$

Pearson R: 0,99724

R-Quadrat (COD): 0,99449

Kor. R-Quadrat: 0,99265

308 K

318 K
Arrhenius plot to estimate the activation energy from a linear fit.
NMR experiments with different ratios of the two reactants

Protocol: First a stock solution of 6.305 mg (1.06 mmol) \((3+2H)(PF_6)_2\) in 1.06 ml CD$_3$CN (c = 1.0·10$^{-2}$ mol·l$^{-1}$) was prepared (solution I). Compound \(2(PF_6)_2\) was directly weighed in an NMR tube and dissolved in 0.25 ml CD$_3$CN. Then the stock solution I was added and the conversion followed by $^1$H NMR spectroscopy.

| entry       | A            | B            | C            |
|-------------|--------------|--------------|--------------|
| solution I [ml/µmol] | 0.25/2.54   | 0.25/2.54   | 0.25/2.54   |
| 2(PF$_6$)$_2$ [mg/µmol] | 1.512/2.54  | 14.114/23.75 | 29.378/49.43 |
| CD$_3$CN [ml] | 0.25         | 0.25         | 0.25         |
| ratio \(2^{2+}/(3+2H)^{2+}\) | 1/1         | 9.5/1        | 20/1         |
| reaction time (temperature) | 90 min (298 K) | 5 min (298 K) | 2 min (298 K) |
| conversion to \(3(PF_6)_2\) [%] | 93          | 95          | 99           |

$^1$H NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry B: first measurement after 1.6 min at 298 K
$^1$H NMR spectrum (199.87 MHz, 298 K, CD$_3$CN) for entry B: last measurement after 5 min at 298 K

Plot showing the decrease of (3+2H)(PF$_6$)$_2$ (%) with time
UV-vis experiments

1) Titration of 3 with 3(PF$_6$)$_2$

|                      | solution I       | solution II      |
|----------------------|------------------|------------------|
| [mg/mmol]            | 0.116/3.86·10$^{-4}$ | 3.176/5.38·10$^{-3}$ |
| CH$_3$CN [ml]        | 10               | 0.466            |
| c [mol l$^{-1}$]     | 3.86·10$^{-5}$   | 1.15·10$^{-2}$   |

Protocol: A 1 cm quartz cuvette equipped with a silicon septum was filled with 3.0 ml of stock solution I (1.15·10$^{-4}$ mmol). Then portions of 5 µl of stock solution II (5.75·10$^{-5}$ mmol/0.5 eq.) were added, the mixture stirred for 1 min, and an UV-vis spectrum recorded.

UV-vis spectra

![UV-vis spectra graph](image-url)
2) Degradation of a mixture of $\text{2} + 2\text{(PF}_6\text{)}_2$

|                | solution I | solution II |
|----------------|------------|-------------|
| $[\text{mg/mmol}]$ | 0.282/9.25$\cdot 10^{-4}$ | 0.463/7.8$\cdot 10^{-4}$ |
| $\text{CH}_3\text{CN [ml]}$ | 10         | 10          |
| $c \text{[mol$\cdot$l}^{-1}$] | $9.26\cdot10^{-5}$ | $7.8\cdot10^{-5}$ |

Protocol: 1.25 ml of solution I (1.16$\cdot 10^{-4}$ mmol), 0.2 ml CH$_3$CN and 1.5 ml solution II (1.17$\cdot 10^{-4}$ mmol) were mixed under stirring in a 1 cm quartz cuvette equipped with a silicon septum. UV-vis spectra were taken after constant time intervals.

**UV-vis spectra**
3) Degradation of a mixture of $3 + 3(\text{PF}_6)_2$

|                  | solution I          | solution II         |
|------------------|---------------------|---------------------|
| $[\text{mg/mmol}]$ | $0.116/3.86 \cdot 10^{-4}$ | $3.176/5.38 \cdot 10^{-3}$ |
| $\text{CH}_3\text{CN [ml]}$ | 10                  | 0.466               |
| $c [\text{mol} \cdot \text{l}^{-1}]$ | $3.86 \cdot 10^{-5}$ | $1.15 \cdot 10^{-2}$ |

Protocol: Under stirring a 1 cm quartz cuvette equipped with a silicon septum was filled with 3.0 ml of solution I ($1.16 \cdot 10^{-4}$ mmol), and 10 µl solution II ($1.15 \cdot 10^{-4}$ mmol). UV-vis spectra were taken after constant time intervals.

**UV-vis spectra**
20  Details of the recycling of 1(PF₆)₂

1. Separation from the reaction product

Separation of (1+2H)X₂ and traces of unreacted (1)X₂ (X⁻ = ClO₄⁻, BF₄⁻ or PF₆⁻) from the reaction mixtures was carried out for the oxidative coupling of N-ethylcarbazole to N,N'-diethyl-3,3'-bicarbazole (see Scheme 1 in the paper), oxidative coupling of 3,3''-dimethoxy-3',4'-dimethyl-o-terphenyl to 3,10-dimethoxy-6,7-dimethylytriphenylene (Scheme 2 in the paper) and reaction of 1(PF₆)₂ with 9,10-dihydroanthracene (AnH₂, Scheme 4 in the paper). In all cases the residue, containing the reaction products, was collected in diethylether and filtrated, allowing the isolation of the coupling product or anthracene in the filtrate. The residue in the filter, consisting of (1+2H)X₂ (X⁻ = ClO₄⁻, BF₄⁻ or PF₆⁻) together with traces of unreacted PCET reagent (1)X₂, was dissolved in CH₃CN for catalytic re-oxidation to the guanidine PCET reagent (1)X₂.

2. Catalytic re-oxidation to give the PCET reagent

In an O₂ atmosphere, the salt (1+2H)X₂ (X⁻ = PF₆⁻) and the dioxygen-activating catalyst (3 mol% of a 1:1 mixture of CuCl₂ and Cu(H₂O)₆(BF₄)₂) were dissolved in acetonitrile. Quantitative conversion of (1+2H)²⁺ into 1²⁺ according to the reaction equation given below is obtained at room temperature in 22 min.

\[
(1+2H)X₂ + \text{O}_2, \quad 3 \text{ mol\% [CuCl}_2/\text{Cu(H}_2\text{O)}_6(\text{BF}_4)_2] \rightarrow \text{CH}_3\text{CN, r.t., 22 min} \rightarrow (1)X₂ >99\% \text{ yield}
\]

For further details (e.g. catalyst screening), see: U. Wild, F. Schön, H.-J. Himmel, *Angew. Chem.* 2017, 129, 16630–16633; *Angew. Chem. Int. Ed.* 2017, 56, 16410–16413.
21 Details of the quantum chemical calculations

Density functional calculations are performed with the program TURBOMOLE.[1-3] The B3LYP functional [4,5] is used in connection with the def2-SV(P) and def2-TZVP basis sets.[6] For the calculation of the two-electron integrals, the resolution-of-the-identity (RI) approximation [7] is used with the appropriate def2-SV(P) and def2-TZVP auxiliary basis set.[8] Structure optimizations are performed with the def2-SV(P) and def2-TZVP basis sets, the determination of the harmonic vibrational frequencies with the def2-SV(P) basis set only. The electronic excitation energies are obtained by time-dependent density functional calculations.[9,10]

[1] TURBOMOLE V7.2 2017, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
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[3] O. Treutler, R. Ahlrichs, J. Chem. Phys. 1995, 102, 346–354.
[4] A. D. Becke, J. Chem. Phys. 1993, 98, 5648–5652.
[5] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem. 1994, 98, 11623–11627.
[6] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297–3305.
[7] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, Chem. Phys. Lett. 1995, 242, 652–660.
[8] F. Weigend, Phys. Chem. Chem. Phys. 2006, 8, 1057–1065.
[9] R. Bauernschmitt, R. Ahlrichs, Chem. Phys. Lett. 1996, 256, 454–464.
[10] R. Bauernschmitt, M. Häser, O. Treuler, R. Ahlrichs, Chem. Phys. Lett. 1997, 264, 573–578.
Thermodynamics of the reactions

Reactions with 9,10-dihydroanthracene

a) Without inclusion of anions

\[
\begin{align*}
\text{SV(P)} & & \text{TZVP}^a (\varepsilon_r = 1) \\
\Delta_r E / \text{kJ mol}^{-1} & & -94.0 & & -96.0 \\
\Delta_r H (0 \text{ K}) / \text{kJ mol}^{-1} & & -90.2 & & -92.1 \\
\Delta_r G (298 \text{ K}) / \text{kJ mol}^{-1} & & -84.5 & & -86.5 \\
\end{align*}
\]

*a* Thermodynamic contributions with the SV(P) basis set.

\[
\begin{align*}
\text{SV(P)} & & \text{TZVP}^a (\varepsilon_r = 1) \\
\Delta_r E / \text{kJ mol}^{-1} & & -192.2 & & -187.8 \\
\Delta_r H (0 \text{ K}) / \text{kJ mol}^{-1} & & -184.2 & & -179.8 \\
\Delta_r G (298 \text{ K}) / \text{kJ mol}^{-1} & & -176.3 & & -171.9 \\
\end{align*}
\]

*a* Thermodynamic contributions with the SV(P) basis set.
b) With inclusion of anions and solvent-effect (COSMO)

\[ \text{SV(P)} \quad \text{TZVP}^a (\varepsilon_r = 1) \quad \text{TZVP}^a (\varepsilon_r = 37.5) \]

|                  | SV(P) | TZVP\(^a\) (\varepsilon_r = 1) | TZVP\(^a\) (\varepsilon_r = 37.5) |
|------------------|-------|--------------------------------|----------------------------------|
| \( \Delta E \) / kJ mol\(^{-1}\) | -89.3 | -90.3                          | -107.1                           |
| \( \Delta H \) (0 K) / kJ mol\(^{-1}\) | -90.5 | -91.6                          | -108.3                           |
| \( \Delta G \) (298 K) / kJ mol\(^{-1}\) | -86.7 | -87.7                          | -104.5                           |

\(^a\) Thermodynamic contributions with the SV(P) basis set.

\[ \text{SV(P)} \quad \text{TZVP}^a (\varepsilon_r = 1) \quad \text{TZVP}^a (\varepsilon_r = 37.5) \]

|                  | SV(P) | TZVP\(^a\) (\varepsilon_r = 1) | TZVP\(^a\) (\varepsilon_r = 37.5) |
|------------------|-------|--------------------------------|----------------------------------|
| \( \Delta E \) / kJ mol\(^{-1}\) | -216.8 | -207.9                        | -203.5                           |
| \( \Delta H \) (0 K) / kJ mol\(^{-1}\) | -210.9 | -202.0                        | -197.6                           |
| \( \Delta G \) (298 K) / kJ mol\(^{-1}\) | -202.3 | -193.4                        | -189.0                           |

\(^a\) Thermodynamic contributions with the SV(P) basis set.
Thermodynamic contributions with the SV(P) basis set.

|                  | SV(P)  | TZVP<sup>a</sup> (ζ<sub>r</sub> = 1) |
|------------------|--------|-----------------------------------|
| Δ<sub>r</sub>E / kJ mol<sup>-1</sup> | -202.7 | -204.2                            |
| Δ<sub>r</sub>H (0 K) / kJ mol<sup>-1</sup> | -193.0 | -194.5                            |
| Δ<sub>r</sub>G (298 K) / kJ mol<sup>-1</sup> | -182.8 | -184.3                            |

<sup>a</sup> Thermodynamic contributions with the SV(P) basis set.
Reactions with \( p \)-dihydrobenzoquinone

a) Without inclusion of anions

\[
\begin{align*}
\text{SV(P)} & \quad \text{TZVP}^a (\epsilon_r = 1) \\
\Delta E / \text{kJ mol}^{-1} & \quad -137.6 \quad -98.1 \\
\Delta H(0 \text{ K}) / \text{kJ mol}^{-1} & \quad -131.1 \quad -91.6 \\
\Delta G(298 \text{ K}) / \text{kJ mol}^{-1} & \quad -125.9 \quad -86.4 \\
\end{align*}
\]

\( ^a \) Thermodynamic contributions with the SV(P) basis set.

b) With inclusion of anions and solvent-effect (COSMO)

\[
\begin{align*}
\text{SV(P)} & \quad \text{TZVP}^a (\epsilon_r = 1) & \quad \text{TZVP}^a (\epsilon_r = 37.5) \\
\Delta E / \text{kJ mol}^{-1} & \quad -162.2 \quad -118.2 \quad -106.5 \\
\Delta H(0 \text{ K}) / \text{kJ mol}^{-1} & \quad -157.8 \quad -113.7 \quad -102.0 \\
\Delta G(298 \text{ K}) / \text{kJ mol}^{-1} & \quad -151.9 \quad -107.8 \quad -96.1 \\
\end{align*}
\]

\( ^a \) Thermodynamic contributions with the SV(P) basis set.
Thermodynamic contributions with the SV(P) basis set.

|                | SV(P) | TZVP<sup>a</sup> (ε<sub>r</sub> = 1) |
|----------------|-------|------------------------------------|
| Δ<sub>g</sub>E / kJ mol<sup>-1</sup> | -148.1 | -114.5                             |
| Δ<sub>g</sub>H (0 K) / kJ mol<sup>-1</sup> | -139.9 | -106.3                             |
| Δ<sub>g</sub>G (298 K) / kJ mol<sup>-1</sup> | -132.3 | -98.7                              |

<sup>a</sup> Thermodynamic contributions with the SV(P) basis set.
PCET reaction between $2^{2+}$ and $(1+2H)^{2+}$

a) Without inclusion of anions

![Diagram showing the PCET reaction between $2^{2+}$ and $(1+2H)^{2+}$]

|                | SV(P) | TZVP<sup>a</sup> ($\varepsilon_r = 1$) |
|----------------|-------|----------------------------------------|
| $\Delta_r E$ / kJ mol<sup>-1</sup> | -98.2 | -91.9                                  |
| $\Delta_r H$ (0 K) / kJ mol<sup>-1</sup> | -94.0 | -87.6                                  |
| $\Delta_r G$ (298 K) / kJ mol<sup>-1</sup> | -91.8 | -85.4                                  |

<sup>a</sup> Thermodynamic contributions with the SV(P) basis set.

b) With inclusion of anions and solvent-effect (COSMO)

![Diagram showing the PCET reaction between $2^{2+}$ and $(1+2H)^{2+}$ with anions and solvent-effect (COSMO)]

|                | SV(P) | TZVP<sup>a</sup> ($\varepsilon_r = 1$) | TZVP<sup>a</sup> ($\varepsilon_r = 37.5$) |
|----------------|-------|----------------------------------------|------------------------------------------|
| $\Delta_r E$ / kJ mol<sup>-1</sup> | -127.5 | -117.6                                  | -96.4                                    |
| $\Delta_r H$ (0 K) / kJ mol<sup>-1</sup> | -120.3 | -110.4                                  | -89.2                                    |
| $\Delta_r G$ (298 K) / kJ mol<sup>-1</sup> | -115.6 | -105.7                                  | -84.5                                    |

<sup>a</sup> Thermodynamic contributions with the SV(P) basis set.
PCET reaction between $2^{2+}$ and $(3+2H)^{2+}$

a) Without inclusion of anions

\[ \text{Scheme 1} \]

| & SV(P) & TZVP$^a$ ($\varepsilon_r = 1$) |
|---|---|---|
| $\Delta E$ / kJ mol$^{-1}$ | 42.5 | -40.7 |
| $\Delta H$ (0 K) / kJ mol$^{-1}$ | 41.8 | -39.9 |
| $\Delta G$ (298 K) / kJ mol$^{-1}$ | 42.0 | -40.2 |

$^a$ Thermodynamic contributions with the SV(P) basis set.

b) With inclusion of anions

\[ \text{Scheme 2} \]

| & SV(P) & TZVP$^a$ ($\varepsilon_r = 1$) |
|---|---|---|
| $\Delta E$ / kJ mol$^{-1}$ | -82.9 | -74.5 |
| $\Delta H$ (0 K) / kJ mol$^{-1}$ | -77.4 | -69.0 |
| $\Delta G$ (298 K) / kJ mol$^{-1}$ | -66.7 | -58.2 |

$^a$ Thermodynamic contributions with the SV(P) basis set.
Coordinates for calculated structures at $\varepsilon = 1$
B3LYP/def2-TZVP

$1^{2+}$

Illustration of the structure (H atoms omitted)

Energy = -1676.926440383 Hartree

Coordinates in Å

|   | N    |       |       |   | N    |       |       |   | N    |       |       |   | N    |       |       |   | N    |       |       |   | C    |       |       |   | C    |       |       |   | C    |       |       |   | H    |       |       |   | H    |       |       |   | H    |       |       |   | C    |       |       |   | H    |       |       |   | H    |       |       |
|---|------|-------|-------|---|------|-------|-------|---|------|-------|-------|---|------|-------|-------|---|------|-------|-------|---|------|-------|-------|---|------|-------|-------|---|------|-------|-------|---|------|-------|-------|---|------|-------|-------|---|------|-------|-------|
|   | 5.3772867 | 7.3699338 | 8.3767889 |   | 3.8360846 | 8.2844509 | 9.8727273 |   | 3.3813576 | 8.2312167 | 7.5758568 |   | 8.7624617 | 10.7760595 | 8.7475595 |   | 7.9670280 | 12.8458069 | 8.0760325 |   | 7.6756392 | 12.1474345 | 10.2925420 |   | 6.6000361 | 7.7991042 | 8.5803999 |   | 8.3286301 | 9.5383382 | 8.7697759 |   | 6.9867568 | 9.1375096 | 8.7281761 |   | 6.2198912 | 9.9021776 | 8.7056338 |   | 4.2199469 | 7.9978313 | 8.6049172 |   | 4.4995917 | 7.6597256 | 11.0139421 |   | 4.9329797 | 6.7089529 | 10.7165890 |   | 3.7574466 | 7.4829469 | 11.7930043 |   | 5.2857942 | 8.3005971 | 11.4235906 |   | 2.8851651 | 9.3425836 | 10.2102493 |   | 2.6712117 | 9.9574383 | 9.3413948 |   | 3.3340720 | 9.9766461 | 10.9781302 |
H 1.9501614 8.9422016 10.6075390
C 1.9250117 8.0850933 7.6759011
H 1.6435133 7.6954791 8.6488934
H 1.5985088 7.3701700 6.9183523
H 1.4104028 9.0309588 7.4993198
C 3.8979275 8.2097120 6.2085378
H 4.9332924 8.5357859 6.185378
C 3.3027603 8.8921227 5.6015026
C 3.8293986 7.2071652 5.7775804
C 8.0997767 11.9019550 9.0289925
C 8.1396190 12.4785407 6.6716632
C 8.0846814 14.2831234 8.1251011
C 8.0846814 14.6890755 7.7074293
C 8.3659323 14.4589089 9.3788646
C 8.1835715 11.3655129 11.4166072
H 7.5120408 10.5398027 11.6694026
C 8.2681127 12.0198585 12.2847455
H 9.1654918 10.9666860 11.1777893
C 6.5764179 13.0561884 10.6145665
C 6.9212564 13.9434837 11.1495097
C 5.8699822 12.5272726 11.2582974
H 6.0545488 13.3615917 9.7128265
N 10.6269274 8.9009081 8.9527135
N 12.1702708 7.9875887 7.4582929
N 12.6214544 8.0384407 9.7559549
N 7.2420440 5.4947937 8.5807887
N 8.0380073 3.4252841 9.2524588
N 8.3297127 4.1238089 7.0360806
C 9.4042676 8.4717478 8.7484222
H 7.6757310 6.7325305 8.5587029
C 9.0175827 7.1333645 8.6003422
H 9.7844725 6.3687209 8.6226970
C 11.7845444 8.2729784 8.7257641
C 11.5084849 8.6134905 6.3167161
H 11.0743083 9.5637831 6.6145073
H 12.2518769 8.7914105 5.5391041
H 10.7231625 7.9728694 5.9050032
C 13.1219331 6.9300083 7.1211565
H 13.3343834 6.3140825 7.986245
H 12.6744884 6.2968766 6.3516711
H 14.0576025 7.3310040 6.7260654
C 14.0779892 8.1844980 9.6584933
H 14.3611538 8.5752506 8.6864347
H 14.4033089 8.8984820 10.4174472
H 14.5921892 7.2383561 9.8347996
C 12.1026165 8.0584519 11.1224450
H 11.0671178 7.7326115 11.1415182
H 12.6965964 7.3751629 11.7296679
C 12.1706916 9.0604825 11.5547205
C 7.9050693 4.3691075 8.2994672
C 7.8649391 3.7923720 10.6568230
H 6.8232169 3.6770587 10.9683467
(1+2H)^2+

Illustration of the structure (C-H atoms omitted)

Energy = -1678.160534386 Hartree

Coordinates in Å
N 5.3391681  7.2848772  8.5215870
H 5.3636149  6.2796399  8.3509642
N 3.8944039  8.8683377  9.4865823
| Element | X    | Y    | Z    |
|---------|------|------|------|
| H       | 12.232110 | 7.2842050 | 5.7607097 |
| H       | 10.8058535 | 6.4921328 | 6.4524662 |
| C       | 13.0622245 | 6.3285719 | 8.1144651 |
| H       | 13.3554306 | 6.3402899 | 9.1602339 |
| H       | 12.5781376 | 5.3734079 | 7.9023064 |
| H       | 13.9529675 | 4.0467630 | 7.4876447 |
| C       | 14.2614150 | 8.9429502 | 9.0339561 |
| H       | 14.3293561 | 8.7071195 | 7.9764708 |
| H       | 14.6297969 | 9.9592379 | 9.1829181 |
| H       | 14.8957303 | 8.2602536 | 9.6018690 |
| C       | 12.6022907 | 9.5509860 | 10.7601517 |
| H       | 11.6409338 | 9.2366679 | 11.1573485 |
| H       | 13.3821506 | 9.2702280 | 11.4685857 |
| H       | 12.6160312 | 10.6388846 | 10.6518718 |
| C       | 7.7347686 | 4.3946558 | 8.1547878 |
| C       | 7.2992194 | 3.1409093 | 10.202837 |
| H       | 6.2182633 | 3.1066246 | 10.3708038 |
| H       | 7.7431996 | 2.2406374 | 10.6304155 |
| H       | 7.6987450 | 4.0153018 | 10.7070493 |
| C       | 7.3692977 | 1.9435598 | 8.0609801 |
| H       | 8.1500159 | 1.2041072 | 8.2524206 |
| H       | 6.4168060 | 1.5228736 | 8.3938383 |
| H       | 7.3036027 | 2.1220933 | 6.9921503 |
| C       | 7.9794895 | 5.3292513 | 5.8886680 |
| H       | 8.6700622 | 6.1700840 | 5.7770609 |
| H       | 7.9367805 | 4.7940815 | 4.9369881 |
| H       | 6.9916551 | 5.7293919 | 6.1017789 |
| C       | 9.4834216 | 3.5154652 | 6.6073728 |
| H       | 9.2107606 | 2.7801544 | 5.8449515 |
| H       | 10.3193070 | 4.1009776 | 6.2128055 |
| H       | 9.8217271 | 2.9894823 | 7.4959700 |
Illustration of the structure (H atoms omitted)

Energy = -954.2570088263 Hartree

Coordinates in Å

|   |   |   |   |
|---|---|---|---|
| N | -0.7063698 | -2.0952223 | 12.6924688 |
| C | 0.4534723 | -2.4619936 | 13.2431629 |
| C | -0.7807956 | -1.6313667 | 11.2988135 |
| C | -1.9686378 | -1.9986718 | 13.4395347 |
| N | 1.6080522 | -2.1596044 | 12.5509123 |
| N | 0.5427902 | -3.2195847 | 14.3391338 |
| H | -0.7831850 | -0.5405186 | 11.2493468 |
| H | -1.7110746 | -2.0002701 | 10.8688296 |
| H | 0.0510444 | -2.0252361 | 10.7225680 |
| H | -2.6593277 | -2.7970962 | 13.1665834 |
| H | -2.4291640 | -1.0435675 | 13.1857630 |
| H | -1.7863496 | -2.0186992 | 14.5091189 |
| C | 2.3497210 | -1.1165276 | 12.6634388 |
| C | 1.8147883 | -3.3686241 | 15.0601402 |
| C | -0.4601459 | -4.2450101 | 14.6862928 |
| C | 2.1307136 | -0.0169416 | 13.6056960 |
| C | 3.5162480 | -1.0290760 | 11.7764245 |
| H | 2.4151898 | -4.1720102 | 14.6274673 |
| H | 1.5864412 | -3.6168318 | 16.0949382 |
| H | 2.3839102 | -2.4446321 | 15.0559862 |
| H | -0.9990494 | -3.9826605 | 15.5965393 |
| H | 0.0705037 | -5.1826897 | 14.8522852 |
| H | -1.1588029 | -4.3927958 | 13.8701329 |
| H | 1.2720004 | -0.0606855 | 14.2643226 |
| C | 2.9693031 | 1.0279707 | 13.6481956 |
| C | 4.3547910 | 0.0158696 | 11.8188757 |
| H | 3.6676859 | -1.8541380 | 11.0921254 |
| C | 4.1355922 | 1.1156192 | 12.7608907 |
(2+2H)^2+

Illustration of the structure (C-H atoms omitted)

Energy = -955.5276406660 Hartree

Coordinates in Å

\[
\begin{array}{ccc}
\text{N} & -0.2997228 & -2.0642835 \ 0.6975157 & -0.5342400 & -0.4702389 \ -0.1883796 & -1.5312197 \ -1.5704292 & -1.7774722 \ 1.9947079 & -2.4587309 \ 0.4608517 & -3.7047322 \ -0.0911803 & -0.4440495 \ -1.0949517 & -1.7952383
\end{array}
\]
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| H    | -2.390357 | -2.356059 | 13.2727197 |
| H    | -1.7950498 | -0.7178187 | 13.5666343 |
| H    | -1.4915467 | -1.9853986 | 14.7612344 |
| H    | 2.6356060 | -3.2337242 | 13.3895373 |
| C    | 2.5908306 | -1.2039400 | 12.9978796 |
| C    | 1.4418746 | -4.0891895 | 15.5292596 |
| C    | -0.7214900 | -4.5746301 | 14.4299628 |
| C    | 2.1310086 | -0.0095846 | 13.5499060 |
| C    | 3.7069681 | -1.1841037 | 12.1620075 |
| H    | 1.9998692 | -4.9796529 | 15.2285290 |
| H    | 0.9063356 | -4.3198646 | 16.4498899 |
| H    | 2.1299235 | -3.2714848 | 15.7271994 |
| H    | -1.4125961 | -4.3795755 | 15.2507495 |
| H    | -0.3861602 | -5.6100386 | 14.4985662 |
| H    | -1.2310606 | -4.4406398 | 13.4809429 |
| H    | 1.2862313 | -0.0020181 | 14.2254961 |
| C    | 2.7784427 | 1.1836454 | 13.2638361 |
| C    | 4.3544524 | 0.0091251 | 11.8759909 |
| H    | 4.0641749 | -2.1020842 | 11.7113843 |
| C    | 3.8945039 | 1.2035061 | 12.4278563 |
| H    | 2.4212098 | 2.1016270 | 13.7144273 |
| H    | 5.1992587 | 0.0015184 | 11.2004466 |
| N    | 4.4901741 | 2.4583966 | 12.1220048 |
| H    | 3.8490265 | 3.2332728 | 12.0368118 |
| C    | 5.7868112 | 2.7324715 | 11.8065294 |
| N    | 6.7851548 | 2.0646373 | 12.396843 |
| N    | 6.0217655 | 3.7045594 | 10.9162902 |
| C    | 6.6760160 | 1.5316572 | 13.7608697 |
| C    | 8.0549913 | 1.7782911 | 11.7217210 |
| C    | 5.0390492 | 4.0883509 | 9.8948662 |
| C    | 7.2039231 | 4.5748999 | 10.9906884 |
| H    | 6.5793397 | 0.4444391 | 13.7522488 |
| H    | 7.5832386 | 1.7961643 | 14.3050923 |
| H    | 5.8243204 | 1.9677373 | 14.2739669 |
| H    | 8.8758408 | 2.3580260 | 12.1458760 |
| H    | 8.2803982 | 0.7188137 | 11.8534961 |
| H    | 7.9743456 | 1.9857808 | 10.6588888 |
| H    | 4.4812952 | 4.9787880 | 10.1961141 |
| H    | 5.5730932 | 4.3187968 | 8.9733068 |
| H    | 4.3509119 | 3.2703870 | 9.6983385 |
| H    | 7.8938582 | 4.3797758 | 10.1689317 |
| H    | 6.8681134 | 5.6101592 | 10.9221899 |
| H    | 7.7149688 | 4.4414646 | 11.9389938 |
Illustration of the structure (H atoms omitted)

Energy = -951.8854033714 Hartree

Coordinates in Å

\begin{align*}
\text{N} & : -1.3780068, 9.0570172, 6.0944071 \\
\text{C} & : -2.4165962, 8.2043387, 6.3281864 \\
\text{C} & : -1.3103464, 9.9742513, 5.1938992 \\
\text{N} & : -2.3839569, 6.9234249, 5.9836960 \\
\text{N} & : -3.4925160, 8.5154429, 7.0542878 \\
\text{C} & : -0.0892282, 10.7874522, 5.1662608 \\
\text{C} & : -2.3447292, 10.2619560, 4.1988273 \\
\text{C} & : -3.5994552, 6.2367310, 6.4571222 \\
\text{C} & : -1.3883845, 6.2599634, 5.1547409 \\
\text{C} & : -4.2338757, 7.2822816, 7.3901847 \\
\text{C} & : -3.7080364, 9.7373695, 7.8181542 \\
\text{H} & : 0.6619087, 10.5600726, 5.9119026 \\
\text{C} & : 0.0822937, 11.7639512, 4.2641287 \\
\text{C} & : -2.1734421, 11.2388285, 3.2970491 \\
\text{H} & : -3.2511473, 9.6696465, 4.2052937 \\
\text{H} & : -3.3350263, 5.3139107, 6.9716401 \\
\text{H} & : -4.2380173, 5.9901520, 5.6061167 \\
\text{H} & : -1.7892920, 6.0471993, 4.1614083 \\
\text{H} & : -1.1011547, 5.3204983, 5.6266753 \\
\text{H} & : -0.5063823, 6.8894424, 5.0667972 \\
\text{H} & : -5.2991807, 7.4205212, 7.2132703 \\
\text{H} & : -4.0824692, 7.0456657, 8.4461172 \\
\text{H} & : -3.5067891, 9.5621923, 8.8777221 \\
\text{H} & : -4.7433052, 10.0570096, 7.7028705 \\
\text{H} & : -3.0522391, 10.5261721, 7.4610833 \\
\text{C} & : -0.9519674, 12.0514760, 3.2688884 \\
\text{H} & : 0.9887558, 12.3561892, 4.2575852
\end{align*}
Energy = -953.1405316858 Hartree

Coordinates in Å

N  2.6553347  0.8101912  -0.4942124
C  1.3234575  0.3652408  -0.2389467
C  3.8197527  0.1950616  -0.1838485
C  0.3252287  0.6889878  -1.1560288
C  0.9915698  -0.3215970  0.9270841
N  4.9191423  0.8796029  0.1460725
H  0.5777838  1.2054950  -2.0736655

Illustration of the structure (C-H atoms omitted)
9,10-Dihydroanthracene (AnH₂)

Illustration of the structure

Energy = -540.5756602807 Hartree

Coordinates in Å

|   |   |   |
|---|---|---|
| C | -3.5517567 | -0.6950504 | 0.5093367 |
| C | -3.5516430 | 0.6952968 | 0.5095286 |
| C | -2.4048958 | -1.3847239 | 0.1333931 |
| C | -2.4047453 | 1.3848866 | 0.1335425 |
| C | -1.2547342 | -0.6995146 | -0.2521256 |
| C | -1.2546816 | 0.6995940 | -0.2521224 |
| C | -0.0000456 | -1.4257459 | -0.6786289 |
| C | 0.0000518 | 1.4257388 | -0.6786426 |
| C | 1.2546978 | -0.6995925 | -0.2521457 |
| C | 1.2547499 | 0.6995115 | -0.2521609 |
| C | 2.4047397 | -1.3848860 | 0.1335907 |
| C | 2.4048842 | 1.3847251 | 0.1334323 |
| C | 3.5516583 | -0.6952925 | 0.5095064 |
| C | 3.5517643 | 0.6950553 | 0.5093242 |
| H | -4.4382069 | -1.2407360 | 0.8082978 |
| H | -4.4378866 | 1.2410446 | 0.8089893 |
| H | -2.4009959 | 2.4691637 | 0.1429655 |
| H | -2.4007389 | 2.4693260 | 0.1431965 |
| H | -0.0000534 | -1.5174611 | -1.7746783 |
| H | -0.0000755 | -2.4466647 | -0.2920560 |
| H | 0.0000445 | 1.5174423 | -1.7746929 |
| H | 0.0000890 | 2.4466616 | -0.2920804 |
| H | 2.4006904 | -2.4693241 | 0.1433832 |
| H | 2.4009384 | 2.4691636 | 0.1431306 |
| H | 4.4379420 | -1.2410376 | 0.8088531 |
| H | 4.4382329 | 1.2407437 | 0.8082254 |
Anthracene (An)

Illustration of the structure

Energy = -539.3765823014 Hartree

Coordinates in Å

|   |   |   |   |
|---|---|---|---|
| C | -3.6481434 | -0.7109626 | -0.0000216 |
| C | -3.6481435 | 0.7109624 | -0.0001442 |
| C | -2.4721345 | -1.4020408 | 0.0000805 |
| C | -2.4721347 | 1.4020406 | -0.0001289 |
| C | -1.2195522 | -0.7201705 | 0.0000941 |
| C | -1.2195524 | 0.7201702 | 0.0000272 |
| C | 0.0000002 | -1.3988299 | 0.0001660 |
| C | -0.000003 | 1.3988302 | 0.0001538 |
| C | 1.2195524 | -0.7201699 | 0.0000568 |
| C | 1.2195523 | 0.7201708 | 0.0001142 |
| C | 2.4721344 | -1.4020405 | -0.0001016 |
| C | 2.4721349 | 1.4020408 | 0.0001057 |
| C | 3.6481433 | -0.7109627 | -0.0001600 |
| C | 3.6481436 | 0.7109624 | -0.0000189 |
| H | -4.5915081 | -1.2427992 | -0.0000030 |
| H | -4.5915082 | 1.2427990 | -0.0002437 |
| H | -2.4716422 | -2.4859510 | 0.0001640 |
| H | -2.4716423 | 2.4859508 | -0.0002238 |
| H | 0.0000005 | -2.4836567 | 0.0002142 |
| H | -0.000005 | 2.4836570 | 0.0002054 |
| H | 2.4716417 | -2.4859507 | -0.0002148 |
| H | 2.4716428 | 2.4859510 | 0.0001599 |
| H | 4.5915079 | -1.2427994 | -0.0002882 |
| H | 4.5915083 | 1.2427988 | 0.0000072 |
**p-Dihydro-benzoquinone**

Illustration of the structure

Energy = -382.6309021723 Hartree

Coordinates in Å

| C   | 1.3959206  | -0.0293616 | 0.0000988 |
|-----|------------|------------|------------|
| C   | 0.7162670  | 1.1861318  | 0.0002096  |
| C   | -0.6727162 | 1.2169398  | 0.0001333  |
| C   | -1.3959207 | 0.0293617  | 0.0000212  |
| C   | -0.7162671 | -1.1861319 | 0.0000233  |
| C   | 0.6727162  | -1.2169396 | 0.0001504  |
| O   | 2.7650095  | -0.1165930 | -0.0002520 |
| H   | 1.2716448  | 2.1181840  | 0.0001779  |
| H   | -1.2048008 | 2.1591512  | -0.0000759 |
| O   | -2.7650095 | 0.1165929  | -0.0000579 |
| H   | -1.2716449 | -2.1181843 | -0.0001015 |
| H   | 1.2048009  | -2.1591508 | 0.0002536  |
| H   | 3.1445676  | 0.7689073  | -0.0004212 |
| H   | -3.1445675 | -0.7689075 | -0.0001595 |
\textit{p}-Benzoquinone

Illustration of the structure

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{benzoquinone_structure.png}
\end{figure}

Energy = -381.3976586665 Hartree

Coordinates in Å
\begin{verbatim}
C  1.4394615 -0.0000004  -0.0002648
C  0.6681633  1.2661677   0.0003196
C -0.6681607  1.2661685   0.0003945
C -1.4394562  0.0000005  -0.0001927
C -0.6681624 -1.2661682   0.0003165
C  0.6681617 -1.2661680   0.0003486
O  2.6573346 -0.0000015  -0.0014168
H  1.2539444  2.1774916   0.0004059
H -1.2539457  2.1774944   0.0005065
O -2.6573381  0.0000017  -0.0012447
H -1.2539460 -2.1774949   0.0003697
H  1.2539435 -2.1774914   0.0004575
\end{verbatim}
Calculations in the context of the TD-DFT calculations for 2, 2⁺ and 2²⁺

2⁺

Illustration of the structure (C-H atoms omitted)

Energy = -954.5791788698

Coordinates in Å

| Atom | X (Å) | Y (Å) | Z (Å) |
|------|-------|-------|-------|
| C    | -0.9746466 | -0.5134201 | -0.8648086 |
| C    | 0.3440485  | -0.7304163 | 1.1381192  |
| C    | 1.3802165  | -0.2223415 | -0.2937311 |
| C    | 0.9746466  | 0.5134201  | 0.8648086  |
| C    | -0.3440485 | 0.7304163  | 1.1381192  |
| C    | -1.3802165 | 0.2223415  | 0.2937311  |
| H    | -1.7319530 | -0.896220  | -1.5410543 |
| H    | 0.6452856  | -1.2900397 | -2.0144217 |
| H    | 1.7319530  | 0.896220   | 1.5410543  |
| H    | -0.6452856 | 1.2900397  | 2.0144217  |
| N    | 2.6475415  | -0.5226535 | -0.6047154 |
| N    | -2.6475415 | 0.5226535  | 0.6047154  |
| C    | 3.7357685  | 0.1117220  | -0.1720375 |
| C    | -3.7357685 | -0.1117220 | 0.1720375  |
| N    | 3.8725660  | 1.4632918  | -0.2597121 |
| N    | 4.7753553  | -0.6262578 | 0.2759694  |
| N    | -3.8725660 | -1.4632918 | 0.2597121  |
| N    | -4.7753553 | 0.6262578  | -0.2759694 |
| C    | 3.0564517  | 2.2504430  | -1.1784019 |
| H    | 2.2135848  | 2.7259818  | -0.6690736 |
| H    | 3.6805068  | 3.0318984  | -1.6153650 |
| H    | 2.6781253  | 1.6196941  | -1.9777773 |
| C    | 4.7011968  | 2.2447556  | 0.6548349  |
| H    | 5.5558168  | 2.6995584  | 0.1480740  |
| H    | 4.0917151  | 3.0478072  | 1.0769235  |
| H    | 5.0586375  | 1.6236350  | 1.4708388  |
| C    | 4.5524011  | -2.0150561 | 0.6713515  |
| H    | 4.6753587  | -2.6920498 | -0.1786441 |
|   |   |   |   |
|---|---|---|---|
| H | 5.2792462 | -2.2783400 | 1.4405039 |
| H | 3.5520989 | -2.1381875 | 1.0742492 |
| C | 6.1721218 | -0.2844695 | 0.0067022 |
| H | 6.7273544 | -0.0935373 | 0.9272856 |
| H | 6.6426669 | -1.1244944 | -0.5089638 |
| H | 6.2362330 | 0.5859825 | -0.6387859 |
| C | -4.7011968 | -2.2447556 | -0.6548349 |
| H | -4.0917151 | -3.0478072 | -1.0769235 |
| H | -5.5558168 | -2.6995584 | -0.1480740 |
| H | -5.0586375 | -1.6236350 | -1.4708388 |
| C | -3.0564517 | -2.2504430 | 1.1784019 |
| H | -3.6805068 | -3.0318984 | 1.6153650 |
| H | -2.2135848 | -2.7259818 | 0.6690736 |
| H | -2.6781253 | -1.6196941 | 1.9777773 |
| C | -4.5524011 | 2.0150561 | -0.6713515 |
| H | -5.2792462 | 2.2783400 | -1.4405039 |
| H | -4.6753587 | 2.6920498 | 0.1786441 |
| H | -3.5520989 | 2.1381875 | -1.0742492 |
| C | -6.1721218 | 0.2844695 | -0.0067022 |
| H | -6.6426669 | 1.1244944 | 0.5089638 |
| H | -6.7273544 | 0.0935373 | -0.9272856 |
| H | -6.2362330 | 0.5859825 | 0.6387859 |
Electronic transitions of $2^+ (^2A_g)$ found in the TD-DFT calculations (B3LYP/TZVP), IRREP $a_u$
Only electronic transitions above 300 nm are listed

| $\lambda$/nm | oscillator strength | leading contribution              | leading contribution  |
|--------------|---------------------|-----------------------------------|-----------------------|
| 542.6        | 0.0451              | $41a_u (\beta) \rightarrow 42a_g (\beta)$ | 54.6%                 |
| 501.3        | 0.186               | $40a_u (\beta) \rightarrow 42a_g (\beta)$ | 68.7%                 |
| 467.9        | 0.00425             | $39a_u (\beta) \rightarrow 42a_g (\beta)$ | 58.3%                 |
| 364.9        | 0.495               | $42a_g (\alpha) \rightarrow 42a_u (\alpha)$ | 82.0%                 |
| 346.3        | 0.141               | $42a_g (\alpha) \rightarrow 43a_u (\alpha)$ | 92.5%                 |

Simulation of the electronic excitation spectrum of $2^+ (^2A_g)$
Isodensity plots for the relevant orbitals of $2^+ (^2A_g)$. Contour values for the isodensity plots are $\pm 0.02$ Bohr$^{(3/2)}$.

$\lambda = 542.6$ nm (54.6% $41a_u (\beta) \rightarrow 42a_g (\beta)$)

$\lambda = 501.3$ nm (68.7% $40a_u (\beta) \rightarrow 42a_g (\beta)$)

$\lambda = 467.9$ nm (58.3% $39a_u (\beta) \rightarrow 42a_g (\beta)$)
\[ \lambda = 364.9 \text{ nm} \ (82.0\% \ 42a_g (\alpha) \rightarrow 42a_u (\alpha)) \]

\[ \lambda = 346.3 \text{ nm} \ (92.5\% \ 42a_g (\alpha) \rightarrow 43a_u (\alpha)) \]
The neutral compound exhibits no electronic transitions in the visible region. First two lowest energetic electronic transitions of $2 \ (^{1}A_g)$ found in the TD-DFT calculations (B3LYP/TZVP), IRREP $a_u$.

| $\lambda$/nm | oscillator strength |
|--------------|---------------------|
| 298.6        | 0.673               |
| 292.2        | 0.0228              |

Simulation of the electronic excitation spectrum of $2 \ (^{1}A_g)$

![Simulation of the electronic excitation spectrum of 2 (1A_g)](image-url)
Electronic transitions of \( {2^2}^+ (^1\text{A}_g) \) found in the TD-DFT calculations (B3LYP/TZVP), IRREP \( \text{a}_u \)

Only electronic transitions above 300 nm are listed

| \( \lambda / \text{nm} \) | oscillator strength | leading contribution | \( \text{HOMO-1} \rightarrow \text{LUMO} \) | \( \text{HOMO-2} \rightarrow \text{LUMO} \) |
|--------------------------|----------------------|-----------------------|-----------------------------------|-----------------------|
| 522.3                    | 0.00359              | 41\text{a}_u \rightarrow 42\text{a}_g | 98.8%                             |
| 398.5                    | 0.0121               | 40\text{a}_u \rightarrow 42\text{a}_g | 59.9%                             |

Simulation of the electronic excitation spectrum of \( {2^2}^+ (^1\text{A}_g) \)