Supplementary Information for

Stable radical versus reversible σ-bond formation of (porphyrinyl)dicyanomethyl radicals

B. Adinarayana,[a] Daiki Shimizu,[a] Ko Furukawa,[b] and Atsuhiro Osuka[a]*

[a] Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan.

[b] Center for Instrumental Analysis, Niigata University, Nishi-ku, Niigata 950-2181, Japan.

Contents

1. General information
2. Synthesis and spectral characterization
3. Mass spectral analysis
4. NMR spectral analysis
5. Single crystal X-ray structure and analysis
6. EPR spectral analysis
7. SQUID measurements
8. Electronic absorption spectral analysis
9. Cyclic voltammograms
10. DFT calculations
1. General Information:

Reagents and materials for the synthesis were purchased from commercial suppliers (reagent grade quality) and were used without further purification unless stated. The main precursor meso-bromoporphyrin 4, meso,β,β′-trichloroporphyrin 5, meso,β-dihaloporphyrins (6,7) and β-bromoporphyrin 16, β,β′-dihaloporphyrins 17-19 were synthesized according to the reported procedures.\[^{[S1,2]}\] Silica gel column chromatography was performed on Wako-gel C300 unless otherwise noted. Alumina column chromatography was performed on Sumitomo γ-Alumina KCG-1525W (Blockmann grade II). Thin-layer chromatography was carried out on aluminium sheets coated with silica gel 60 F254 (Merck 5554). High-resolution atmospheric-pressure-chemical-ionization time-of-flight mass spectrometry (HR-APCI-TOFMS) was recorded on a BRUKER micrOTOF model using positive mode. The NMR solvent CDCl\textsubscript{3} was purified by passing through a short pad of aluminum oxide prior to use. \(^1\text{H},\) and \(^{13}\text{C}\) NMR spectra were recorded on a JEOL ECA600 spectrometer, and chemical shifts were reported in ppm (\(\delta\) scale) relative to internal standards CHCl\textsubscript{3} (\(\delta = 7.26\) ppm for \(^1\text{H}, 77.23\) ppm for \(^{13}\text{C}\)). UV/Visible absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Single crystal X-ray diffraction analysis data were collected at \(-180 \, ^\circ C\) with a Rigaku XtaLAB P200 by using graphite monochromated Cu-K\(\alpha\) radiation (\(\lambda = 1.54187\) Å). The structures were solved by direct methods (SHELXT) and refined with full-matrix least square technique (SHELXL-2014/7).\[^{[S3]}\] EPR spectra were recorded on a Bruker E500 spectrometer at Institute for Molecular Science, Okazaki, Japan. SQUID measurements were conducted by using a Quantum Design MPMS-2 system in Research Center for Low Temperature and Materials Sciences, Kyoto University. Redox potentials were measured by the cyclic voltammetry and differential pulse voltammetry method on an ALS660 electrochemical analyzer model. DFT calculations were performed using the Gaussian 09 program package at (U)B3LYP/6-311G* level.\[^{[S4]}\]
2. Synthesis and spectral characterization:

Scheme S1. Synthesis of 8-15. (i) 10 equiv. malononitrile, 10 equiv. NaH, DMI, 60 °C, 1 h. (ii) 200 equiv. PbO₂, CH₂Cl₂, rt, 2 h.

Scheme S2. Synthesis of 20-27. For Synthesis of 20 (i) 5 equiv. malononitrile, 8 equiv. NaH, DME, Pd(PPh₃)₄ (20 mol%), 80 °C, 2 h. For synthesis of 21-23 (ii) 10 equiv. malononitrile, 10 equiv. NaH, DMI, 100 °C, 6 h. (iii) 200 equiv. PbO₂, CH₂Cl₂, rt, 2 h.
2a. General procedure for the synthesis of 8-11:

A 25 ml Schlenk tube was loaded with meso-halogenated porphyrins 8-11 (20 mg), malononitrile (10 eq) and sodium hydride (60% in oil, 10eq), which was kept under N₂ atmosphere. The mixture was dissolved in dry 1,3-dimethyl-2-imidazolidinone (DMI) (3 mL), and the resulting solution was stirred at 60 °C for 1 h. After the completion of the reaction, the mixture was quenched with 1M HCL aq. and the resulting crude mixture was filtered. The precipitate was collected and further purified by column chromatography using silica gel (C300, in CH₂Cl₂:n-hexane:Et₂O 1:3:1) to afford target molecules in 66-70% yield.

Synthesis of 8:

According to the general procedure, starting from meso-bromoporphyrin 4 (20 mg, 0.02 mmol), malononitrile (13.2 mg, 0.20 mmol) and sodium hydride (60% in oil, 8 mg, 0.20 mmol) the compound 8 was synthesized and purified by column chromatography using silica gel (C300, in CH₂Cl₂:n-hexane:Et₂O 1:3:1) to afford target molecule 8 in 65% yield (13 mg, 0.013 mmol).

¹H NMR (600 MHz, CDCl₃); δ/ ppm = 9.35 (d, J = 4.9 Hz, 2H, β), 8.97 (d, J = 4.9 Hz, 2H, β), 8.78 (m, 4H, β), 7.83 (m, 6H, meso-Ar), 7.76 (m, 2H), 7.73 (m, 1H, meso-Ar), 7.01 (s, 1H, meso-CH(CN)₂), 1.49 (s, 36H, tBu) and 1.46 (s, 18H, tBu). ¹³C NMR (151 MHz, CDCl₃); δ/ppm = 149.46, 149.36, 143.84, 143.22, 142.66, 140.17, 139.32, 139.32, 135.47, 133.77, 133.22, 128.84, 128.71, 127.25, 127.71, 126.79, 121.62, 113.91, 35.21, 35.18, 31.86 and 31.83.

HR-APCI-TOFMS: m/z calcd for [C₆₅H₇₂NiO₅⁺]⁺ = 994.5172; found = 994.5180 ([M⁺]); UV-Vis (CH₂Cl₂): λ_max(nm) (ε×10⁵ [M⁻¹cm⁻¹]) = 418 (2.02), 534 (0.15), 568 (0.07).

Synthesis of 9:

Ar¹ = 3,5-di-tert-butylphenyl
According the general procedure, starting from meso,β,β’-trichloroporphyrin 5 (20 mg, 0.019 mmol), malononitrile (12.5 mg, 0.19 mmol) and sodium hydride (60% in oil, 7.6 mg, 0.19 mmol) the compound 9 was synthesized and purified by column chromatography using silica gel (C300, in CH₂Cl₂:n-hexane:Et₂O 1:3:1) to afford target molecule 9 in 68% yield (14 mg, 0.013 mmol).

\(^1\)H NMR (600 MHz, CDCl₃); δ/ppm = 8.75 (s, 2H, β), 8.71 (d, J = 4.9 Hz, 2H, β), 8.67 (d, J = 4.9 Hz, 2H, β), 7.75 (d, J = 1.8 Hz, 2H, meso-Ar), 7.74 (t, J = 1.8 Hz, 2H, meso-Ar), 7.72 (d, J = 1.8 Hz, 4H, meso-Ar), 7.71 (s, 1H, meso-Ar), 7.37 (s, 1H, meso-CH(CN)₂), 1.47 (s, 36H, tBu) and 1.45 (s, 18H, tBu).

\(^13\)C NMR (151 MHz, CDCl₃); δ/ppm = 149.79, 149.67, 143.53, 143.20, 138.49, 138.31, 135.36, 134.68, 133.86, 128.58, 128.53, 122.22, 121.97, 121.44, 113.12, 35.23, 31.86, 31.85 and 31.82.

HR-APCI-TOFMS: m/z calcd for [C₆₅H₇₀Cl₂N₆⁵Ni]⁺ = 1062.4392; found = 1062.4363 (\[M⁺\]).

UV-Vis (CH₂Cl₂): \(λ_{max} (\text{nm}) (ε×10^5 \text{ [M}^{-1}\text{cm}^{-1}]) = 428 (1.78), 551 (0.15), 591 (0.08).

Synthesis of 10:

According the general procedure, starting from meso-chloro,β-bromoporphyrin 6 (20 mg, 0.019 mmol), malononitrile (12.5 mg, 0.19 mmol) and sodium hydride (60% in oil, 7.6 mg, 0.19 mmol) the compound 10 was synthesized and purified by column chromatography using silica gel (C300, in CH₂Cl₂:n-hexane:Et₂O 1:3:1) to afford target molecule 10 in 70% yield (14.5 mg, 13.5 µmol).

\(^1\)H NMR (600 MHz, CDCl₃); δ/ppm = 9.63 (d, J = 5.1 Hz, 1H, β), 8.93 (s, 1H, β), 8.90 (d, J = 5.1 Hz, 1H, β), 8.74 (m, 3H, β), 8.65 (d, J = 5.0 Hz, 1H, β), 7.96 (s, 1H, meso-CH(CN)₂), 7.79 (d, J = 1.8 Hz, 2H, meso-Ar), 7.78 (d, J = 1.8 Hz, 2H, meso-Ar), 7.74 (dd, J = 3.8, 1.8 Hz, 4H, meso-Ar), 7.71 (t, J = 1.8 Hz, 1H, meso-Ar), 1.48 (s, 36H, tBu) and 1.45 (s, 18H, tBu).

\(^13\)C NMR (151 MHz, CDCl₃); δ/ppm = 149.66, 149.64, 149.54, 149.31, 143.91, 143.43, 143.38, 143.28, 141.93, 139.97, 138.90, 138.87, 139.71, 135.83, 134.33, 133.04, 133.72, 133.50, 130.34, 128.77, 128.71, 128.64, 123.00, 122.07, 121.96, 121.90, 121.84, 120.95, 114.22, 35.30 – 35.14 (m) and 31.85 (d). HR-APCI-TOFMS: m/z calcd for [C₆₅H₇₀BrN₆⁵Ni]⁺ = 1072.4277; found = 1072.4279 (\[M⁺\]); UV-Vis (CH₂Cl₂): \(λ_{max} (\text{nm}) (ε×10^5 \text{ [M}^{-1}\text{cm}^{-1}]) = 423 (2.23), 544 (0.15), 580 (0.08).
Synthesis of 11:

According the general procedure, starting from meso-chloro,β-iodoporphyрин 7 (20 mg, 0.018 mmol), malononitrile (12 mg, 0.18 mmol) and sodium hydride (60% in oil, 7.2 mg, 0.18 mmol) the compound 11 was synthesized and purified by column chromatography using silica gel (C300, in CH$_2$Cl$_2$-n-hexane:Et$_2$O 1:3:1) to afford target molecule 11 in 69% yield (14 mg, 12.5 µmol).

$^1$H NMR (600 MHz, CDCl$_3$); δ/ ppm = 9.64 (d, $J = 5.2$ Hz, 1H, β), 9.17 (s, 1H, β), 8.89 (d, $J = 5.2$ Hz, 1H, β), 8.76 – 8.72 (m, 3H, β), 8.65 (d, $J = 4.8$ Hz, 1H, β), 7.95 (s, 1H, meso-CH(CN)$_2$), 7.78 (m, 4H, meso-Ar), 7.75 (m, 4H, meso-Ar), 7.71 (m, 1H, meso-Ar), 1.48 (m, 36H, tBu) and 1.45 (s, 18H, tBu). $^{13}$C NMR (151 MHz, CDCl$_3$); δ/ppm = 149.64, 149.54, 147.03, 143.88, 143.47, 143.30, 142.03, 143.88, 143.47, 143.30, 142.03, 141.93, 138.91, 138.70, 135.73, 134.31, 133.98, 133.74, 133.54, 130.52, 128.85, 128.78, 128.64, 122.91, 122.03, 121.95, 121.83, 114.28, 97.33, 35.23 and 31.86. HR-APCI-TOFMS: $m/z$ calcd for [C$_{65}$H$_{71}$IN$_{6}$Ni]$^+$ = 1120.4138; found = 1120.4141 ([M$^+$]).

UV-Vis (CH$_2$Cl$_2$): λ$_{max}$ (nm) ($\varepsilon \times 10^5$ [M$^{-1}$cm$^{-1}$]) = 425 (1.97), 544 (0.14), 581 (0.07).

Synthesis of 20:

A 25 ml Schlenk tube was loaded with sodium hydride (60% in oil, 6 mg, 0.15 mmol) and 3ml Dimethoxyethane (DME) solvent and kept under N$_2$ atmosphere. After 10 min malononitrile (6.25 mg, 0.094 mmol) was added and the reaction mixture was stirred for 20 more min. To the reaction mixture β-Br porphyrин 16 (20 mg, 0.018 mmol) and Pd(PPh$_3$)$_4$ (4.4 mg, 3.78 µmol) was added and the resulting solution was stirred at 80 °C for 2 h. After the completion of the reaction, the mixture was quenched with 1M HCL aq. and the resulting crude mixture was extracted with CH$_2$Cl$_2$, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The compound was purified by column chromatography using silica gel (C300, in CH$_2$Cl$_2$:n-hexane:Et$_2$O 1:3:1) to afford target molecule 20 in 74% yield (14 mg, 0.014 mmol).
1H NMR (600 MHz, CDCl3); δ/ppm = 9.71 (s, 1H, meso-H), 9.16 (d, J = 4.8 Hz, 1H, β), 9.13 (s, 1H, β), 8.93 (d, J = 4.7 Hz, 1H, β), 8.85 – 8.80 (m, 4H, β), 7.89 – 7.88 (m, 2H, meso-Ar), 7.88 – 7.87 (m, 2H, meso-Ar), 7.86 – 7.85 (m, 2H, meso-Ar), 7.79 (m, 1H, meso-Ar), 7.77 – 7.75 (m, 1H, meso-Ar), 7.74 – 7.72 (m, 1H, meso-Ar), 6.52 (s, 1H, meso-CH(CN)2), 1.51 (s, 18H, tBu), 1.49 (s, 18H, tBu) and 1.47 (s, 18H, tBu); 13C NMR (151 MHz, CDCl3); δ/ppm = 149.60, 149.43, 149.31, 144.34, 143.33, 142.97, 139.75, 139.40, 137.23, 133.69, 133.43, 133.329, 133.06, 133.00, 132.91, 129.00, 128.89, 121.93, 121.83, 121.63, 121.61, 121.58, 120.76, 112.30, 99.96, 35.34 – 35.16 (m), 31.91 (s), 23.26 and 23.24. HR-APCI-TOFMS: m/z calcd for [C65H72N68Ni]+ = 994.5172; found = 994.5131 ([M]+); UV-Vis (CH2Cl2): λmax (nm) (ε×10^5 [M^-1 cm^-1]) = 414 (2.80), 526 (0.20), 558 (0.07).

**Synthesis of 21:**

A 25 ml Schlenk tube was loaded with β-halogenated porphyrins 17 (20 mg, 0.018 mmol), malononitrile (12 mg, 0.35 mmol) and sodium hydride (60% in oil, 7.3 mg, 0.18 mmol) was kept under N2 atmosphere. The mixture was dissolved in dry 1,3-Dimethyl-2-imidazolidinone (DMI) 3 mL, and the resulting solution was stirred at 100 °C for 6 h. After the completion of the reaction, the mixture was quenched with 1M HCL aq. and the resulting crude mixture was filtered. The precipitate was collected and further purified by column chromatography using silica gel (C300, in CH2Cl2:n-hexane:Et2O 1:3:1) to afford target molecule 21 in 68% yield (13.5 mg, 12.6 µmol).

1H NMR (600 MHz, CDCl3); δ/ppm = 9.82 (s, 1H, meso-H), 9.14 (d, J = 0.7 Hz, 1H, β), 8.92 (s, 1H, β), 8.87 – 8.80 (m, 4H, β), 7.89 (d, J = 1.8 Hz, 2H, meso-Ar), 7.86 (d, J = 1.8 Hz, 2H, meso-Ar), 7.84 (d, J = 1.8 Hz, 2H, meso-Ar), 7.80 (t, J = 1.8 Hz, 1H, meso-Ar), 7.78 (t, J = 1.8 Hz, 1H, meso-Ar), 7.75 (t, J = 1.8 Hz, 1H, meso-Ar), 6.55 (s, 1H, meso-CH(CN)2), 1.53 (s, 18H, tBu), 1.51 (s, 18H, tBu) and 1.48 (s, 18H, tBu). 13C NMR (151 MHz, CDCl3); δ/ppm = 149.68, 149.57, 149.38, 144.35, 144.13, 144.00, 143.68, 142.57, 140.20, 139.66, 139.11, 137.81, 134.01, 133.68, 133.62, 133.37, 133.13, 129.25, 128.85, 128.83, 126.07, 122.33, 122.23, 122.13, 121.93, 120.65, 120.42, 112.23, 98.34, 35.35 – 35.16 (m) and 31.89 (d). HR-APCI-TOFMS: m/z calcd for [C65H71BrN68Ni]+ = 1072.4277; found = 1072.4224 ([M]+); UV-Vis (CH2Cl2): λmax (nm) (ε×10^5 [M^-1 cm^-1]) = 416 (2.31), 526 (0.17), 558 (0.05).
Synthesis of 22:

According the general procedure, starting from $\beta,\beta$-diiodo-porphyrin 18 (20 mg, 0.017 mmol), malononitrile (11.2 mg, 0.17 mmol) and sodium hydride (60% in oil, 6.8 mg, 0.17 mmol) the compound 22 was synthesized and purified by column chromatography using silica gel (C300, in CH$_2$Cl$_2$:n-hexane:Et$_2$O 1:3:1) to afford target molecule 22 in 74% yield (14.2 mg, 12.7 $\mu$mol).

$^1$H NMR (600 MHz, CDCl$_3$); $\delta$/ppm = 9.77 (s, 1H, meso-H), 9.13 (s, 1H, $\beta$), 9.11 (s, 1H, $\beta$), 8.84 – 8.78 (m, 4H, $\beta$), 7.87 (d, $J$ = 1.6 Hz, 2H, meso-Ar), 7.84 (d, $J$ = 1.6 Hz, 2H, meso-Ar), 7.83 (d, $J$ = 1.6 Hz, 2H, meso-Ar), 7.79 (t, $J$ = 1.6 Hz, 1H, meso-Ar), 7.77 (t, $J$ = 1.6 Hz, 1H, meso-Ar), 6.59 (s, 1H, meso-CH(CN)$_2$), 1.51 (s, 18H, tBu), 1.50 (s, 18H, tBu) and 1.47 – 1.45 (m, 18H, tBu). $^{13}$C NMR (151 MHz, CDCl$_3$); $\delta$/ppm = 149.68, 149.54, 149.37, 144.34, 144.31, 144.05, 143.64, 141.63, 141.50, 140.18, 139.23, 138.13, 133.67, 133.63, 133.57, 129.24, 128.88, 128.83, 126.12, 122.24, 122.04, 121.90, 121.69, 112.25, 100.81, 35.34 – 35.16 (m, 18H, tBu) and 31.98 – 31.80 (m). HR-APCI-TOFMS: $m$/z calcd for [C$_{65}$H$_{71}$IN$_6$]$^{58}$Ni$^+$ = 1120.4138; found = 1120.4156 ([M]$^+$); UV-Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$(nm) ($\epsilon \times 10^5$ [M$^{-1}$cm$^{-1}$]) = 418 (2.39), 530 (0.18), 561 (0.04).

Synthesis of 23:

According the general procedure, starting from $\beta,\beta$-diiodo-porphyrin 19 (20 mg, 0.019 mmol), malononitrile (12.5 mg, 0.19 mmol) and sodium hydride (60% in oil, 7.6 mg, 0.19 mmol) the compound 23 was synthesized and purified by column chromatography using silica gel (C300, in CH$_2$Cl$_2$:n-hexane:Et$_2$O 1:3:1) to afford target molecule 23 in 78% yield (14.6 mg, 0.015 mmol).
\(^1\)H NMR (600 MHz, CDCl\(_3\)); \(\delta/\text{ppm} = 9.79\ (s, 1\text{H, meso-}\text{H}), 8.93\ (s, 1\text{H, }\beta), 8.88\ (d, J = 0.6\ \text{Hz, 1H, }\beta), 8.75\ (m, 2\text{H, }\beta), 8.60\ (dd, J = 4.9, 1.4\ \text{Hz, 2H, }\beta), 7.87\ (d, J = 1.8\ \text{Hz, 2H, meso-}\text{Ar}), 7.74\ (t, J = 1.4\ \text{Hz, 1H, meso-}\text{Ar}), 7.24\ (d, J = 1.4\ \text{Hz, 4H, meso-}\text{Ar}), 6.59\ (s, 1\text{H, meso-}\text{CH(CN)}\_2), 2.59\ (d, J = 3.0\ \text{Hz, 6H, Me}), 1.80\ (d, J = 1.6\ \text{Hz, 12H, Me})\) and 1.47 (s, 18H, tBu).

\(^1\)C NMR (151 MHz, CDCl\(_3\)); \(\delta/\text{ppm} = 149.34, 144.70, 144.37, 143.98, 143.37, 141.84, 140.13, 139.85, 139.64, 139.15, 138.62, 138.45, 136.48, 136.27, 134.25, 133.87, 132.35, 132.30, 131.48, 128.34, 128.21, 126.74, 122.07, 121.64, 119.30, 117.20, 112.29, 100.83, 92.69, 35.25, 31.87, 23.21 and 21.62 (d).

HR-APCI-TOFMS: \(m/z\) calced for \([\text{C}_{55}\text{H}_{51}\text{IN}_{58}\text{Ni}]^+ = 980.2573;\) found = 980.2529 ([M]\(^+\)); UV-Vis (CH\(_2\)Cl\(_2\)): \(\lambda_{\text{max}}(\text{nm}) (\varepsilon \times 10^5 [\text{M}^{-1}\text{cm}^{-1}]) = 416 (2.46), 528 (0.19), 561 (0.07).

**Synthesis of 12:**

The CH\(_2\)Cl\(_2\) solution of a precursor 8 (20 mg, 0.02 mmol), 9 (20 mg, 18.8 \(\mu\)mol), 10 (20 mg, 18.8 \(\mu\)mol) or 11 (20 mg, 17.8 \(\mu\)mol) was kept under nitrogen atmosphere and added excess amount of PbO\(_2\) (200 eq). The resulting solution was allowed to stir at room temperature for 2 h. After completion, the reaction mixture was filtered through celite and concentrated by a rotary evaporator. The compound was purified by column chromatography using silica gel (C300, in CH\(_2\)Cl\(_2\):n-hexane (2:5) afforded the respective stable radical 12 (14 mg 0.014 mmol, 70% Yield), 13 (14 mg 0.013 mmol, 70% Yield), 14 (13 mg 0.012 mmol, 65% Yield) or 15 (12.5 mg 0.011 mmol, 63% Yield).

This compound was synthesized and purified according to the general procedure.

HR-APCI-TOFMS: \(m/z\) calced for \([\text{C}_{65}\text{H}_{71}\text{N}_{65}\text{Ni}]^+ = 993.5094;\) found = 993.5037 ([M]\(^+\)); UV-Vis (CH\(_2\)Cl\(_2\)): \(\lambda_{\text{max}}(\text{nm}) (\varepsilon \times 10^5 [\text{M}^{-1}\text{cm}^{-1}]) = 466 (0.90), 537 (0.22), 638 (0.26), 804 (0.06).

**Synthesis of 13**

This compound was synthesized and purified according to the general procedure.
HR-APCI-TOFMS: \(m/z\) calcd for [C_{65}H_{67}Cl_{2}N_{6}^{58}Ni]^+ = 1061.4314; found = 1061.4273 ([M]^+);
UV-Vis (CH\(_2\)Cl\(_2\)): \(\lambda_{\text{max}}\) (\(\varepsilon\times10^5\) [M\(^{-1}\)cm\(^{-1}\)]) = 451 (0.53), 472 (0.54), 537 (0.22), 636 (0.16), 855 (0.08), and 1600 (0.012).

**Synthesis of 14:**

This compound was synthesized and purified according to the general procedure.

HR-APCI-TOFMS: \(m/z\) calcd for [C_{65}H_{70}^{79}BrN_{6}^{58}Ni]^+ = 1071.4199; found = 1071.4147 ([M]^+);
UV-Vis (CH\(_2\)Cl\(_2\)): \(\lambda_{\text{max}}\) (\(\varepsilon\times10^5\) [M\(^{-1}\)cm\(^{-1}\)]) = 468 (0.67), 539 (0.21), 638 (0.19), 850 (0.06).

**Synthesis of 15:**

This compound was synthesized and purified according to the general procedure.

HR-APCI-TOFMS: \(m/z\) calcd for [C_{65}H_{70}N_{6}^{58}Ni]^+ = 1119.4060; found = 1119.4007 ([M]^+);
UV-Vis (CH\(_2\)Cl\(_2\)): \(\lambda_{\text{max}}\) (\(\varepsilon\times10^5\) [M\(^{-1}\)cm\(^{-1}\)]) = 469 (0.66), 536 (0.21), 640 (0.18), 848 (0.06).

**Synthesis of 24-27:**

The CH\(_2\)Cl\(_2\) solution of a precursor 20 (20 mg, 0.02 mmol), 21 (20 mg, 18.6 \(\mu\)mol), 22 (20 mg, 17.8 \(\mu\)mol) or 23 (20 mg, 0.02 mmol), was kept under nitrogen atmosphere and added excess amount of PbO\(_2\) (200 eq). The resulting solution was allowed to stir at room temperature for 2 h. After completion, the reaction mixture was filtered through celite and concentrated by a rotary evaporator. The compound was purified by column chromatography using silica gel (C300, in CH\(_2\)Cl\(_2\):n-hexane (2:7) afforded the respective stable radical 24 (10 mg 0.01 mmol, 50% Yield), 25 (12 mg 0.011 mmol, 60% Yield), 26 (12 mg 0.011 mmol, 60% Yield) or 27 (14 mg 0.014 mmol, 71% Yield).
Synthesis of \((24)_2\):

\[
\begin{align*}
&\text{Ar}^1 \\
\text{N} & \text{N} \text{N} \\
\text{N} & \text{N} \text{N} \\
\text{CN} & \text{CN} \\
\text{CN} & \text{CN} \\
&\text{Ar}^1 \\
\end{align*}
\]

\[
\begin{align*}
\text{PbO}_2 & \rightarrow \text{CH}_2\text{Cl}_2 \\
\end{align*}
\]

\[\text{50\%} \quad \text{Ar}^1 = \text{3,5-di-tert-butylphenyl}\]

\(\text{1H NMR (600 MHz, 213 K, CDCl}_3\); \(\delta/\text{ppm} = 9.22 (\text{s, 1H, meso-H}), 9.02 (\text{s, 1H, meso-H}), 8.91 - 8.74 (\text{m, 5H, } \beta), 8.59 (\text{d, } J = 4.3 \text{ Hz, 1H, } \beta), 8.47 (\text{m, 2H, } \beta), 8.41 (\text{d, } J = 4.3 \text{ Hz, 1H, } \beta), 8.37 - 8.27 (\text{m, 4H, } \beta), 8.22 - 8.09 (\text{m, 3H, meso-Ar}), 7.97 (\text{m, 2H, } \beta, \text{ meso-Ar}), 7.82 - 7.57 (\text{m, 7H, meso-Ar}), 7.46 - 7.30 (\text{m, 4H, meso-Ar}), 7.15 (\text{d, } J = 24.8 \text{ Hz, 2H, meso-Ar}), 1.88 (\text{s, 6H, tBu}), 1.73 (\text{s, 3H, tBu}), 1.68 (\text{s, 6H, tBu}), 1.61 (\text{s, 6H, tBu}), 1.58 - 1.48 (\text{m, 30H, tBu}), 1.37 - 1.23 (\text{m, 42H, tBu}), 1.23 - 1.19 (\text{m, 6H, tBu}) \text{ and } 0.65 (\text{s, 3H, tBu}); \text{HR-APCI-TOFMS: } m/z \text{ calcd for } [\text{C}_{65}\text{H}_{71}\text{N}_{6}\text{Ni}]^+ = 993.5094; \text{ found } = 993.5096 ([M]^+); \text{UV-Vis (CH}_2\text{Cl}_2): \lambda_{\text{max (nm)}} (\varepsilon \times 10^5 [\text{M}^{-1}\text{cm}^{-1}]) = 415 (1.20), 490 (0.22), 683 (0.11), 1000-1450 (broad).
\]

Synthesis of \((25)_2\):

\[
\begin{align*}
&\text{Ar}^1 \\
\text{N} & \text{N} \text{N} \\
\text{N} & \text{N} \text{N} \\
\text{NC} & \text{CN} \\
\text{CN} & \text{CN} \\
&\text{Ar}^1 \\
\end{align*}
\]

\[
\begin{align*}
\text{PbO}_2 & \rightarrow \text{CH}_2\text{Cl}_2 \\
\end{align*}
\]

\[\text{60\%} \quad \text{Ar}^1 = \text{3,5-di-tert-butylphenyl}\]

This compound was synthesized and purified according to the general procedure.

\(\text{1H NMR (600 MHz, 213 K, CD}_2\text{Cl}_2); \delta/\text{ppm} = 10.82 (\text{s, 1H, meso-H}), 8.96 (\text{s, 1H, } \beta), 8.77 (\text{d, } J = 4.8 \text{ Hz, 1H, } \beta), 8.59 - 8.54 (\text{m, 2H, } \beta, \text{ meso-Ar}), 8.45 (\text{d, } J = 5.0 \text{ Hz, 1H, } \beta), 8.39 (\text{d, } J = 11.4 \text{ Hz, 2H, meso-Ar}), 8.21 (\text{s, 1H, }), 8.15 (\text{d, } J = 4.7 \text{ Hz, 1H, } \beta), 8.07 (\text{d, } J = 4.7 \text{ Hz, 1H, } \beta), 7.93 (\text{d, } J = 4.9 \text{ Hz, 2H, } \beta), 7.79 - 7.71 (\text{m, 3H, meso-Ar, } \beta), 7.64 (\text{d, } J = 24.3 \text{ Hz, 4H}), 7.53 (\text{s, 1H}), 7.40 (\text{s, 2H}), 7.27 (\text{s, 1H, meso-Ar}), 7.15 (\text{s, 1H}), 7.00 (\text{d, } J = 23.1 \text{ Hz, 2H}), 6.58 (\text{s, 1H, } \beta), 6.21 (\text{s, 1H, meso-H}), 6.14 (\text{s, 1H}), 5.81 (\text{s, 1H}), 5.62 (\text{s, 1H}), 1.69 (\text{s, 9H, tBu}), 1.62 (\text{s, 9H, tBu}), 1.59 (\text{s, 9H, tBu}), 1.55 (\text{s, 9H, tBu}), 1.46 (\text{s, 9H, tBu}), 1.34 (\text{s, 9H, tBu}), 1.26 (\text{s, 9H, tBu}), 1.17 (\text{s, 9H, tBu}), 1.15 (\text{s, 9H, tBu}), 1.03 (\text{s, 9H, tBu}) \text{ and } 0.91 (\text{s, 9H, tBu}) \text{ and -0.15 (s, 9H, tBu)); HR-APCI-TOFMS: } m/z \text{ calcd for } [\text{C}_{65}\text{H}_{70}\text{BrNi}_{68}\text{Ni}]^+ = 1071.4199; \text{ found } = 1071.4191 ([M]^+); \text{UV-Vis (CH}_2\text{Cl}_2): \lambda_{\text{max (nm)}} (\varepsilon \times 10^5 [\text{M}^{-1}\text{cm}^{-1}]) = 416 (1.03), 488 (0.17), 518 (0.14), 691 (0.08), 1000-1450 (broad).
Synthesis of (26)₂:

This compound was synthesized and purified according to the general procedure.

$^1$H NMR (600 MHz, 233 K, CD$_2$Cl$_2$); $\delta$/ppm = 10.70 (s, 1H, meso-H), 9.13 (s, 1H, $\beta$), 8.73 (d, $J = 4.8$ Hz, 1H, $\beta$), 8.57 (s, 1H, $\beta$), 8.52 (d, $J = 4.9$ Hz, 1H, $\beta$), 8.45 (d, $J = 4.9$ Hz, 1H, $\beta$), 8.42 (s, 2H, $\beta$), 8.21 (s, 1H, meso-Ar), 8.14 (d, $J = 4.7$ Hz, 1H, $\beta$), 8.08 (d, $J = 4.7$ Hz, 1H, $\beta$), 7.94 (m, 2H, $\beta$, meso-Ar), 7.79 (s, 1H, meso-Ar), 7.77 (s, 1H, meso-Ar), 7.73 (s, 1H, meso-Ar), 7.66 (m, 2H, meso-Ar), 7.63 (s, 1H, meso-Ar), 7.60 (d, $J = 4.9$ Hz, 1H, $\beta$), 7.49 (s, 1H, meso-Ar), 7.45 (m, 2H, $\beta$, meso-Ar), 7.29 (s, 1H, meso-Ar), 7.09 (s, 1H, meso-Ar), 7.02 (s, 1H, meso-Ar), 7.00 (s, 1H, meso-Ar), 6.63 (s, 1H, meso-Ar), 6.23 (s, 1H, meso-1H), 6.14 (s, 1H, meso-Ar), 5.99 (s, 1H, meso-Ar), 5.85 (s, 1H, meso-Ar), 1.71 (s, 9H, tBu), 1.62 (s, 18H, tBu), 1.56 (s, 9H, tBu), 1.45 (s, 9H, tBu), 1.35 (s, 9H, tBu), 1.25 (s, 9H, tBu), 1.19 (s, 9H, tBu), 1.16 (s, 9H, tBu), 1.06 (s, 9H, tBu) and -0.14 (s, 9H, tBu); HR-APCI-TOFMS: $m/z$ calcd for [C$_{65}$H$_{30}$In$_6^{58}$Ni]$^+ = 1119.4060$; found = 1119.4040 ([M]$^+$); UV-Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (nm) ($\varepsilon$×10$^5$ [M$^{-1}$cm$^{-1}$]) = 417 (1.23), 488 (0.21), 516 (0.18), 691 (0.09), 1000-1450 (broad).

Synthesis of (27)₂:

This compound was synthesized and purified according to the general procedure.

$^1$H NMR (600 MHz, 193 K, CD$_2$Cl$_2$); $\delta$/ppm = 11.03 (s, 1H, meso-H), 9.23 (s, 1H, $\beta$), 8.98 (s, 1H, $\beta$), 8.76 (d, $J = 4.5$ Hz, 1H, $\beta$), 8.61 (m, 2H, $\beta$, meso-Ar), 8.52 (m, 2H, $\beta$), 8.27 – 8.17 (m, 3H, meso-Ar, $\beta$), 7.96 (s, 1H, meso-Ar), 7.88 (s, 1H, meso-Ar), 7.71 (d, $J = 17.6$ Hz, 2H, meso-Ar), 7.62 (d, $J = 4.6$ Hz, 1H, $\beta$), 7.53 (s, 1H, meso-Ar), 7.48 (s, 1H, meso-Ar), 7.42 (s, 1H, meso-Ar), 7.33 (s, 1H, meso-Ar), 7.12 (d, $J = 19.3$ Hz, 3H, meso-Ar), 6.88 (s, 1H, meso-Ar), 6.73 (s, 2H, meso-Ar), 6.38 (s, 1H, meso-H), 3.12 (s, 1H, meso-Ar), 2.60 (s, 3H, Mesityl), 2.52 (s, 3H, Mesityl), 2.22 (s, 6H, Mesityl), 1.99 (s, 3H, Mesityl), 1.69 (s, 3H, Mesityl), 1.44 (s, 9H, tBu), 1.41 (s, 6H, Mesityl), 1.31 (s, 18H, tBu), 1.12 (s, 9H, tBu), 0.84 (s, 3H, Mesityl) and -2.79 (s, 3H, Mesityl); HR-APCI-TOFMS: $m/z$ calcd for [C$_{55}$H$_{30}$In$_6^{58}$Ni]$^+ = 979.2453$; found = 979.2468 ([M]$^+$); UV-Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (nm) ($\varepsilon$×10$^5$ [M$^{-1}$cm$^{-1}$]) = 414 (1.29), 535 (0.16), 571 (0.08), 687 (0.06), 1000-1450 (broad).
Mass spectral analysis:

![Mass Spectra](image1)

**Figure S1**: HR-APCI-TOF mass spectra of 8 (top: observed, bottom: simulated).

![Mass Spectra](image2)

**Figure S2**: HR-APCI-TOF mass spectra of 9 (top: observed, bottom: simulated).
**Figure S3:** HR-APCI-TOF mass spectra of 10 (top: observed, bottom: simulated).

**Figure S4:** HR-APCI-TOF mass spectra of 11 (top: observed, bottom: simulated).
Figure S5: HR-APCI-TOF-MS of 12 (top: observed, bottom: simulated).

Figure S6: HR-APCI-TOF mass spectra of 13 (top: observed, bottom: simulated).
Figure S7: HR-APCI-TOF mass spectra of 14 (top: observed, bottom: simulated).

Figure S8: HR-APCI-TOF mass spectra of 15 (top: observed, bottom: simulated).
Figure S9: HR-APCI-TOF mass spectra of 20 (top: observed, bottom: simulated).

Figure S10: HR-APCI-TOF mass spectra of 21 (top: observed, bottom: simulated).
Figure S11: HR-APCI-TOF-MS of 22 (top: observed, bottom: simulated).

Figure S12: HR-APCI-TOF mass spectra of 23 (top: observed, bottom: simulated).
**Figure S13**: HR-APCI-TOF mass spectra of 24 (top: observed, bottom: simulated).

**Figure S14**: HR-APCI-TOF mass spectra of 25 (top: observed, bottom: simulated).
**Figure S15:** HR-APCI-TOF mass spectra of 26 (top: observed, bottom: simulated).

**Figure S16:** HR-APCI-TOF mass spectra of 27 (top: observed, bottom: simulated).
4. NMR spectral analysis:

**Figure S17:** $^1$H-NMR spectrum of 8 in CDCl$_3$. (* represents residual solvents and impurity grease).

**Figure S18:** $^{13}$C-NMR spectrum of 8 in CDCl$_3$. (* represents residual solvents and impurity grease).
**Figure S19:** $^1$H-NMR spectrum of 9 in CDCl$_3$. (* represents residual solvents and impurity grease).

**Figure S20:** $^{13}$C-NMR spectrum of 9 in CDCl$_3$. (* represents residual solvents and impurity grease).
Figure S21: $^1$H-NMR spectrum of 10 in CDCl$_3$. (* represents residual solvents and impurity grease).

Figure S22: $^{13}$C-NMR spectrum of 10 in CDCl$_3$. (* represents residual solvents and impurity grease).
Figure S23: $^1$H-NMR spectrum of 11 in CDCl$_3$. (* represents residual solvents and impurity grease).

Figure S24: $^{13}$C-NMR spectrum of 11 in CDCl$_3$. (* represents residual solvents and impurity grease).
Figure S25: $^1$H-NMR spectrum of 20 in CDCl$_3$. (* represents residual solvents and impurity grease).

Figure S26: $^{13}$C-NMR spectrum of 20 in CDCl$_3$. (* represents residual solvents and impurity grease).
Figure S27: $^1$H-NMR spectrum of 21 in CDCl$_3$. (* represents residual solvents and impurity grease).

Figure S28: $^{13}$C-NMR spectrum of 21 in CDCl$_3$. (* represents residual solvents and impurity grease).
**Figure S29:** $^1$H-NMR spectrum of 22 in CDCl$_3$. (* represents residual solvents and impurity grease).

**Figure S30:** $^{13}$C-NMR spectrum of 22 in CDCl$_3$. (* represents residual solvents and impurity grease).
Figure S31: $^1$H-NMR spectrum of 23 in CDCl$_3$. (* represents residual solvents and impurity grease).

Figure S32: $^{13}$C-NMR spectrum of 23 in CDCl$_3$. (* represents residual solvents and impurity grease).
**Figure S33**: LT-1H-NMR spectrum of (24)$_2$ in CDCl$_3$.

**Figure S34**: LT-1H-NMR expanded spectrum of (24)$_2$ in CDCl$_3$. 
Figure S35: LT-$^1$H-NMR spectrum of (25)$_2$ in CD$_2$Cl$_2$.

Figure S36: LT-$^1$H-NMR expanded spectrum of (25)$_2$ in CD$_2$Cl$_2$. 
Figure S37: LT-1H-NMR spectrum of (26)$_2$ in CD$_2$Cl$_2$.

Figure S38: LT-1H-NMR expanded spectrum of (26)$_2$ in CD$_2$Cl$_2$. 
Figure S39: LT-$^1$H-NMR spectrum of (27)$_2$ in CD$_2$Cl$_2$.

Figure S40: LT-$^1$H-NMR expanded spectrum of (27)$_2$ in CD$_2$Cl$_2$. 
5. Single crystal X-ray structure and analysis:

**Figure S41**: Single crystal X-ray structure of 9 and 21. a), c) Top view and b), d) side view and the peripheral hydrogen atoms, the meso-aryl groups in side view are omitted for clarity.

**Figure S42**: Single crystal X-ray structure of 12. a) Top view, b) close interaction between radical pairs. The meso-aryl groups in b) and the peripheral hydrogen atoms in a) and b) are omitted for clarity.
Figure S43: Single crystal X-ray structure of 13. a) Top view, b) molecule present in the unit cell, c) and d) close interaction between radical pairs. The meso-aryl groups in b), c) & d) and the peripheral hydrogen atoms in a)-d) are omitted for clarity.
Figure S44: Single crystal X-ray structure of (27)$_2$. a), c) Top view and b) side view and the peripheral hydrogen atoms in a), b) and c), the meso-aryl groups in b) and d) are omitted for clarity.
Table S1: Crystal data for 9 and 21:

<table>
<thead>
<tr>
<th>Crystal parameters</th>
<th>9</th>
<th>21</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₆₅.₂H₇₀.₂Cl₂.₆N₆NiO₀.₄</td>
<td>C₆₆H₇₃BrCl₂N₆Ni</td>
</tr>
<tr>
<td>M/g mol⁻¹</td>
<td>1095.14</td>
<td>1159.82</td>
</tr>
<tr>
<td>T/K</td>
<td>93</td>
<td>93</td>
</tr>
<tr>
<td>Crystal dimensions/mm³</td>
<td>0.34 × 0.24 × 0.05</td>
<td>0.52 × 0.35 × 0.10</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C₂/c</td>
<td>P₂₁/n</td>
</tr>
<tr>
<td>a/Å</td>
<td>40.0152(8)</td>
<td>11.3078(7)</td>
</tr>
<tr>
<td>b/Å</td>
<td>12.8645(3)</td>
<td>21.1896(11)</td>
</tr>
<tr>
<td>c/Å</td>
<td>23.9666(6)</td>
<td>25.4949(17)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>102.621(2)</td>
<td>100.698(3)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V/Å³</td>
<td>12039.3(5)</td>
<td>6002.6(6)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>ρcalcld/mg m⁻³</td>
<td>1.208</td>
<td>1.283</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>1.864</td>
<td>2.403</td>
</tr>
<tr>
<td>F(000)</td>
<td>4630.0</td>
<td>2432.0</td>
</tr>
<tr>
<td>Reflns. collected</td>
<td>41466</td>
<td>41753</td>
</tr>
<tr>
<td>Indep.reflns.</td>
<td>11807 [R_int = 0.0424,</td>
<td>11695 [R_int = 0.0246,</td>
</tr>
<tr>
<td>[R(int)]</td>
<td>R_sigma = 0.0437]</td>
<td>R_sigma = 0.0192]</td>
</tr>
<tr>
<td>Max/min transmission</td>
<td>1.000/0.653</td>
<td>1.000/0.817</td>
</tr>
<tr>
<td>Data/restraints /parameters</td>
<td>11807/189/811</td>
<td>11695/324/771</td>
</tr>
<tr>
<td>GOF on F²</td>
<td>1.025</td>
<td>1.034</td>
</tr>
<tr>
<td>Final R indices[I &gt; 2σ(I)]</td>
<td>R₁ = 0.0719, wR₂ = 0.2039</td>
<td>R₁ = 0.0819, wR₂ = 0.2541</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0851, wR₂ = 0.2171</td>
<td>R₁ = 0.0863, wR₂ = 0.2591</td>
</tr>
<tr>
<td>Largest diff peak and hole</td>
<td>1.31/-0.71</td>
<td>1.75 and -2.46</td>
</tr>
<tr>
<td>[e Å⁻³]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCDC</td>
<td>1900738</td>
<td>1900741</td>
</tr>
</tbody>
</table>
Table S2: Crystal data for 12, 13 and (27)₂:

<table>
<thead>
<tr>
<th>Crystal parameters</th>
<th>12</th>
<th>13</th>
<th>(27)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₂₀₁H₂₂₇N₁₈Ni₃</td>
<td>C₁₃₃H₁₄₄Cl₁₀N₁₂Ni₂</td>
<td>C₁₁₀H₁₀₀I₂Ni₁₂Ni₂</td>
</tr>
<tr>
<td>M/g mol⁻¹</td>
<td>3071.08</td>
<td>2382.51</td>
<td>1961.2</td>
</tr>
<tr>
<td>T/K</td>
<td>93</td>
<td>93</td>
<td>93</td>
</tr>
<tr>
<td>Crystal dimensions/mm³</td>
<td>0.20 x 0.11 x 0.01</td>
<td>0.15 x 0.12 x 0.02</td>
<td>0.15 x 0.08 x 0.02</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Cm</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
<td>24.352(5)</td>
<td>14.2135(4)</td>
<td>16.4887(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>26.043(4)</td>
<td>17.6443(8)</td>
<td>17.6517(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>16.592(3)</td>
<td>26.4127(11)</td>
<td>18.6605(2)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
<td>76.353(4)</td>
<td>82.3860(10)</td>
</tr>
<tr>
<td>β/°</td>
<td>122.777(3)</td>
<td>82.030(3)</td>
<td>73.3520(10)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
<td>78.350(3)</td>
<td>69.5290(10)</td>
</tr>
<tr>
<td>V/Å³</td>
<td>8847(3)</td>
<td>6275.5(4)</td>
<td>4871.78(10)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>ρ calc’d/mg m⁻³</td>
<td>1.153</td>
<td>1.261</td>
<td>1.337</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.805</td>
<td>2.742</td>
<td>5.869</td>
</tr>
<tr>
<td>F(000)</td>
<td>3286.0</td>
<td>2504.0</td>
<td>2012.0</td>
</tr>
<tr>
<td>Reflns. collected</td>
<td>29723</td>
<td>85166</td>
<td>58669</td>
</tr>
<tr>
<td>Indep. reflns.</td>
<td>13484 [R(int) = 0.0416, R(sigma) = 0.0455]</td>
<td>23864 [R(int) = 0.0900, R(sigma) = 0.0861]</td>
<td>15394 [R(int) = 0.0581, R(sigma) = 0.0445]</td>
</tr>
<tr>
<td>Max/min transmission</td>
<td>1.000/0.796</td>
<td>1.000/0.226</td>
<td>1.000/0.579</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>13484/170/1154</td>
<td>23864/160/1506</td>
<td>15394/185/1238</td>
</tr>
<tr>
<td>GOF on F²</td>
<td>1.038</td>
<td>1.420</td>
<td>1.047</td>
</tr>
<tr>
<td>Final R indices</td>
<td>R₁ = 0.0586, wR₂ = 0.1502</td>
<td>R₁ = 0.1495, wR₂ = 0.3772</td>
<td>R₁ = 0.0686, wR₂ = 0.1871</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0667, wR₂ = 0.1558</td>
<td>R₁ = 0.1945, wR₂ = 0.4111</td>
<td>R₁ = 0.0870, wR₂ = 0.2004</td>
</tr>
<tr>
<td>Largest diff peak and hole [e Å⁻³]</td>
<td>0.63/-0.38</td>
<td>4.20/-1.14</td>
<td>2.54/-1.45</td>
</tr>
<tr>
<td>CCDC</td>
<td>1900739</td>
<td>1905150</td>
<td>1900740</td>
</tr>
</tbody>
</table>
6. EPR spectral analysis:

**Figure S45**: EPR spectral analysis of a) 12, b) 13, c) 14 and d) 15 in toluene at room temperature. (Red lines: observed and blue lines: simulated).
Figure S46 EPR spectral analysis of a) 12, b) 13, c) 14 and d) 15 in toluene at 15 K. (Red lines: observed and blue lines: simulated).

7. SQUID measurements:
Figure S47: Temperature-dependent magnetic susceptibility of a) 12, b) 13, c) 14 and d) 15.
(Blue circles: observed and red lines: simulated).

8. Electronic absorption spectral analysis:
Figure S48: Electronic absorption spectra of 8 and 12 in CH$_2$Cl$_2$.

Figure S49: Electronic absorption spectra of 9 and 13 in CH$_2$Cl$_2$. 
Figure S50: Electronic absorption spectra of 10 and 14 in CH$_2$Cl$_2$.

Figure S51: Electronic absorption spectra of 11 and 15 in CH$_2$Cl$_2$. 
**Figure S52:** LT Electronic absorption spectra of 12 in CH₂Cl₂.

**Figure S53:** HT Electronic absorption spectra of 12 in toluene.
Figure S54: LT Electronic absorption spectra of 13 in CH₂Cl₂.

Figure S55: LT Electronic absorption spectra of 14 in CH₂Cl₂.
**Figure S56:** LT Electronic absorption spectra of 15 in CH₂Cl₂.

**Figure S57:** Electronic absorption spectra of 20 and (24)$_2$ in CH₂Cl₂.
Figure S58: Electronic absorption spectra of 21 and (25)₂ in CH₂Cl₂.

Figure S59: Electronic absorption spectra of 22 and (26)₂ in CH₂Cl₂.
**Figure S60:** Electronic absorption spectra of 23 and (27)$_2$ in CH$_2$Cl$_2$.

**Figure S61:** VT Electronic absorption spectra of (24)$_2$ in toluene. Inset VT EPR spectrum of (24)$_2$ in toluene.
Figure S62: HT Electronic absorption spectra of (25)$_2$ in toluene. Inset VT EPR spectrum of (25)$_2$ in toluene.

Figure S63: HT Electronic absorption spectra of (26)$_2$ in toluene. Inset VT EPR spectrum of (26)$_2$ in toluene.
Figure S64: HT Electronic absorption spectra of (27)$_2$ in toluene. Inset VT EPR spectrum of (27)$_2$ in toluene.

Figure S65: van’t Hoff plots (ln $K_{eq}$ vs $T^{-1}$) for a) 24, b) 25, c) 26 and d) 27 in toluene.
9. Cyclic voltammograms:

**Figure S66:** Cyclic voltammogram of 12 in CH₂Cl₂ (scan rate: 0.05 V/s, supporting electrolyte: 0.1 M Bu₄NPF₆, working electrode: Pt, counter electrode: Pt wire, reference electrode: Ag/0.01 M AgClO₄).
Figure S67: Cyclic voltammogram of 13 in CH₂Cl₂ (scan rate: 0.05 V/s, supporting electrolyte: 0.1 M "Bu₄NPF₆, working electrode: Pt, counter electrode: Pt wire, reference electrode: Ag/0.01 M AgClO₄).

Figure S68: Cyclic voltammogram of 14 in CH₂Cl₂ (scan rate: 0.05 V/s, supporting electrolyte: 0.1 M "Bu₄NPF₆, working electrode: Pt, counter electrode: Pt wire, reference electrode: Ag/0.01 M AgClO₄).
**Figure S69:** Cyclic voltammogram of 15 in CH₂Cl₂ (scan rate: 0.05 V/s, supporting electrolyte: 0.1 M ᵅBu₄NPF₆, working electrode: Pt, counter electrode: Pt wire, reference electrode: Ag/0.01 M AgClO₄).

**Figure S70:** Cyclic voltammogram of (24)₂ in CH₂Cl₂ (scan rate: 0.05 V/s, supporting electrolyte: 0.1 M ᵅBu₄NPF₆, working electrode: Pt, counter electrode: Pt wire, reference electrode: Ag/0.01 M AgClO₄).
**Figure S71:** Cyclic voltammogram of (25)$_2$ in CH$_2$Cl$_2$ (scan rate: 0.05 V/s, supporting electrolyte: 0.1 M $n$Bu$_4$NPF$_6$, working electrode: Pt, counter electrode: Pt wire, reference electrode: Ag/0.01 M AgClO$_4$).

**Figure S72:** Cyclic voltammogram of (26)$_2$ in CH$_2$Cl$_2$ (scan rate: 0.05 V/s, supporting electrolyte: 0.1 M $n$Bu$_4$NPF$_6$, working electrode: Pt, counter electrode: Pt wire, reference electrode: Ag/0.01 M AgClO$_4$). (* represents either impurity or radical formation).

**Figure S73:** Cyclic voltammogram of (27)$_2$ in CH$_2$Cl$_2$ (scan rate: 0.05 V/s, supporting electrolyte: 0.1 M $n$Bu$_4$NPF$_6$, working electrode: Pt, counter electrode: Pt wire, reference electrode: Ag/0.01 M AgClO$_4$). (* represents either impurity or radical formation).
Table S3: Redox potentials of 12-15 and (24)$_2$-(27)$_2$:

<table>
<thead>
<tr>
<th>Compd.</th>
<th>$E_{1/2}^{OX1}$/V</th>
<th>$E_{1/2}^{OX2}$/V</th>
<th>$E_{1/2}^{RED1}$/V</th>
<th>$E_{1/2}^{RED2}$/V</th>
<th>$\Delta E_{HL}$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.26</td>
<td>1.21</td>
<td>-0.33</td>
<td>-2.05</td>
<td>0.59</td>
</tr>
<tr>
<td>13</td>
<td>0.31</td>
<td>1.21</td>
<td>-0.29</td>
<td>-1.95</td>
<td>0.60</td>
</tr>
<tr>
<td>14</td>
<td>0.29</td>
<td>1.22</td>
<td>-0.31</td>
<td>-2.02</td>
<td>0.60</td>
</tr>
<tr>
<td>15</td>
<td>0.28</td>
<td>1.20</td>
<td>-0.30</td>
<td>-1.95</td>
<td>0.58</td>
</tr>
<tr>
<td>(24)$_2$</td>
<td>0.50</td>
<td>1.29</td>
<td>-0.33</td>
<td>-1.99</td>
<td>0.83</td>
</tr>
<tr>
<td>(25)$_2$</td>
<td>0.55</td>
<td>1.33</td>
<td>-0.31</td>
<td>-1.88</td>
<td>0.86</td>
</tr>
<tr>
<td>(26)$_2$</td>
<td>0.55</td>
<td>1.37</td>
<td>-0.30</td>
<td>-1.88</td>
<td>0.85</td>
</tr>
<tr>
<td>(27)$_2$</td>
<td>0.54</td>
<td>1.39</td>
<td>-0.31</td>
<td>-1.96</td>
<td>0.85</td>
</tr>
</tbody>
</table>

10. DFT calculations:

All calculations were carried out using the Gaussian 09 program. The calculations were performed by the density functional theory (DFT) method with UB3LYP level, employing a basis set 6-311G(d). tert-Butyl groups were replaced by hydrogen atoms to simplify calculations.

Figure S74. Spin density distribution plots of 12 (a,b), 13 (c,d), 14 (e,f) and 15 (g,h) calculated at the UB3LYP/6-311G* level (isovalue: 0.001).
**Figure S75.** Spin density distribution plots of β-dicyanomethyl monomer radicals (a,b) 24, (c,d) 25 and (e,f) 26, calculated at the UB3LYP/6-311G* level (isovalue: 0.001).

**Figure S76:** Selected molecular orbitals of 12 calculated at UB3LYP/6-311G(d) .
Figure S77: Selected molecular orbitals of 13 calculated at UB3LYP/6-311G(d).

Figure S78: Selected molecular orbitals of 14 calculated at UB3LYP/6-311G(d).
Figure S79: Selected molecular orbitals of 15 calculated at UB3LYP/6-311G(d).

Figure S80: Selected molecular orbitals of 24-monomer radical calculated at UB3LYP/6-311G(d)
**Figure S81**: Selected molecular orbitals of 25-monomer radical calculated at UB3LYP/6-311G(d).

**Figure S82**: Selected molecular orbitals of 26-monomer radical calculated at UB3LYP/6-311G(d).
Figure S83: Selected molecular orbitals of (24)$_2$ calculated at UB3LYP/6-311G(d).

Figure S84: Selected molecular orbitals of (25)$_2$ calculated at UB3LYP/6-311G(d).
**Figure S85:** Selected molecular orbitals of (27)$_2$ calculated at UB3LYP/6-311G(d).

**Figure S86:** Torsion angles of optimized structure of a) 12, b) 13, c) 14 and d) 15 (in deg.) calculated at UB3LYP/6-311G(d). The meso-aryl groups and the peripheral hydrogen atoms in a)-d) are omitted for clarity.
Figure S87: The comparison between observed absorption spectrum in CH$_2$Cl$_2$ (line) of 12 vs calculated absorption spectrum on the basis of optimized structures (bar).

Figure S88: The comparison between observed absorption spectrum in CH$_2$Cl$_2$ (line) of 13 vs calculated absorption spectrum on the basis of optimized structures (bar).
Figure S89: The comparison between observed absorption spectrum in CH$_2$Cl$_2$ (line) of 14 vs calculated absorption spectrum on the basis of optimized structures (bar).

Figure S90: The comparison between observed absorption spectrum in CH$_2$Cl$_2$ (line) of 15 vs calculated absorption spectrum on the basis of optimized structures (bar).
Supporting references:


