

Supporting Information

"Tschitschibabin type Biradicals": Benzenoid or Quinoid?

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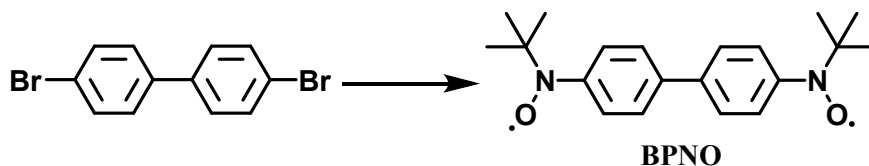
General methods:

EPR spectra were recorded in diluted and oxygen-free solutions of toluene with the concentration of 10^{-4} molar unless otherwise stated by using a Bruker X-band spectrometer ESP300 E, equipped with an NMR gauss meter (Bruker ER035), a frequency counter (Bruker ER 041 XK) and a variable temperature control continuous flow N_2 cryostat (Bruker B-VT 2000). UV-Vis spectra were recorded in toluene solutions with Perkin Elmer Spectrometer (UV/Vis/NIR Lambda 900) by using 1 cm optical-path quartz cell at room temperature. Mass spectra were obtained on FD-MS, VG Instruments ZAB-2 mass spectrometer. The X-ray crystallographic data for the biradical was collected on Nonius Kappa CCD (Mo- $K\alpha$) diffractometer equipped with graphite mono chromator. The structures were solved by direct method (SHELXS) and refined by a full-matrix least-squares procedure.

Synthetic details:

All reagents and chemicals were purchased from Aldrich and Alfa Aesar used for synthesis without further purification unless otherwise specified. 2,7-Diiodo-4,5,9,10-tetramethoxyppyrene and *t*-BuNO were synthesized according to literature procedures.^{32, 33, 48}

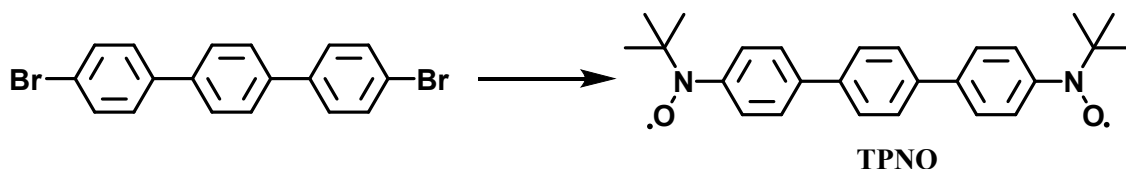
N,N'-([1,1'-Biphenyl]-4,4'-diyl)bis(N-oxy-tert-butylamine) (BPNO):



To a solution of 4,4'-dibromo-1,1'-biphenyl (200 mg, 0.64 mmol) in 5 ml THF, 2.2 equivalent 1.6 M *n*-BuLi hexane solution was added drop wise at -78 °C and stirred for 1 hour at the same temperature. The mixture was gradually warmed to room temperature over the period of 2 hour and further stirred for 30 min. To the resulting mixture the solution of 2-methyl-2-nitrosopropane (*t*-BuNO) dimer (3 equivalents) in 2 ml THF was added drop wise at -78 °C, continued stirring for 2 hour and warmed to room temperature. The reaction mixture was hydrolyzed with aqueous ammonium chloride. Organic layer was separated, washed with water and brine and dried over $MgSO_4$. Solvent was removed under vacuum and residue used as it is for next step without any purification. To the slurry of crude product in 20 ml

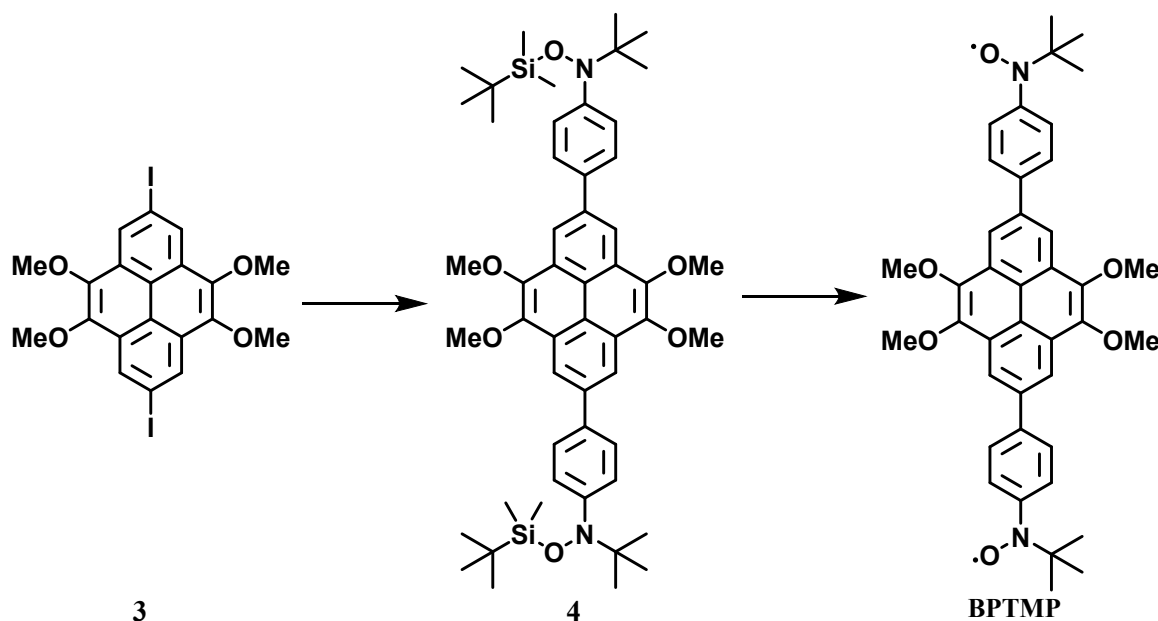
DCM, 300 mg of Ag₂O was added and stirred for 3 hour under argon. The reaction mixture was filtered through celite and the solvent was evaporated, the residue purified over alumina column using hexane:ethylacetate (100:10) as eluent. Yield 60 mg of BPNO (29 % in two steps). MS-FD= 325.9 (100 %), λ_{max} (ϵ , mol⁻¹cm⁻¹) 322 (1.04 X 10⁴), 476 (4.2 X 10⁴), 649 (1171). EPR (353 K, 10⁻⁴ M in toluene): five lines, $g_{\text{iso}} = 2.0067$, $a_{\text{N}}/2 = 6.250$ G.

N,N'-([1,1':4,1''-Terphenyl]-4,4''-diyl)bis(N-oxy-tert-butylamine) (TPNO):



To a solution of 4,4''-dibromo-1,1':4,1''-terphenyl (100 mg, 0.26 mmol) in 40 ml THF, 2.2 equivalent 1.6 M *n*-BuLi hexane solution was added drop wise at -78 °C stirred for 1 hour at same temperature. The mixture was gradually warmed to room temperature over the period of 2 hour and further stirred for 30 min. To the resulting mixture the solution of 2-methyl-2-nitrosopropane (*t*-BuNO) dimer (3 equivalents) in 2 ml THF was added drop wise at -78 °C, continued stirring for 2 hour and warmed to room temperature. The reaction mixture was hydrolyzed with aqueous ammonium chloride. Organic layer was separated, washed with water and brine and dried over MgSO₄. Solvent was removed under vacuum and residue used as it is for next step without any purification. To the slurry of crude product in 40 ml DCM, 200 mg of Ag₂O was added and stirred for 3 hour under argon. The mixture was filtered through celite and solvent evaporated, the residue was purified over alumina column using hexane:ethylacetate (100:25) as eluent. Yield 25 mg of TPNO (24% in two steps). MS-FD= 402.4 (100%). λ_{max} (ϵ , mol⁻¹cm⁻¹) 349 (3.4 X 10⁴). EPR (298 K, 10⁻⁴ M in toluene): five lines, $g_{\text{iso}} = 2.0065$, $a_{\text{N}}/2 = 6.225$ G.

N,N'-((4,5,9,10-Tetramethoxypyrene-2,7-diyl)bis(4,1-phenylene))bis(N-oxy-tert-butylamine) (BPTMP):



To the oven dried Schlenk flask 2,7-diiodo-4,5,9,10-tetramethoxyppyrene (100 mg, 0.17 mmol) and 4-(*tert*-butyl(*tert*-butyldimethylsilyloxy)-amino)phenylboronic acid (140 mg, 2.5 equivalents) were dissolved in 16 ml toluene. To the resulting mixture aqueous solution of Na₂CO₃ (83 mg in 6 ml H₂O) added and mixture was bubbled with argon for 30 min, then 5 mol % Pd(PPh₃)₄ added and the resulting solution heated at 83 °C for 20 hour. The reaction mixture cooled to room temperature and washed with water. The organic layer was separated, and solvent was removed under vacuum. The crude intermediate product **4** was obtained in quantitative yield characterized by FD mass and used as it is for next step. **MS-FD** (8 kV, CH₂Cl₂) m/z: found 877.3 (100 %).

The crude product **4** was dissolved in 15 ml THF. The conc. HCl (1.2 ml) was added and reaction mixture stirred at room temperature for overnight under argon. The reaction mixture poured into 10 ml H₂O and the precipitate formed were filtered, dried and used immediately for next step. The precipitate and excess of Ag₂O (200 mg) were dispersed in 30 ml DCM and stirred at room temperature for 3 hour under argon. The solution passed through the celite, and the solvent was removed under vacuum. The crude product was purified by column chromatography using 1:1 (hexane:DCM) as eluent. Yield 40 mg (39 % in three steps). **MS-FD** (8 kV, CH₂Cl₂) m/z: found 646.6 (100 %). λ_{max} (ϵ , mol⁻¹cm⁻¹) 357 (8.6 X 10⁴). **EPR** (298 K, 10⁻⁴ M in toluene): five lines, $g_{\text{iso}} = 2.0058$, $a_N/2 = 5.948$ G.

Table S1: Crystallographic table.

	BPNO	TPNO	BPTMP
CCDC No.	1001620	1001622	1001621
Formula	C ₁₀ H ₁₃ N ₁ O ₁	C ₂₆ H ₃₀ N ₂ O ₂	C ₄₀ H ₄₂ N ₂ O ₆
Formula Weight	163.22	402.54	646.78
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	P21/a, (No. 14)	P21/a, (No. 14)	C2/c, (No. 15)
a,b,c/Å	8.614(5),9.107(7), 11.338(9)	8.840(2), 8.988(3), 13.346(4)	18.130(8), 11.229(3), 17.613(8)
α,β,γ /°	90, 101.9 (4), 90	90, 94.8(2), 90	90, 113.4(1), 90
V/Å ³	870.21(11)	1056.79(5)	3290.6(2)
Z	4	2	4
D(calc)/g ⁻¹ cm ³	1.246	1.265	1.306
Mu(MoKa)/mm ⁻¹	0.081	0.080	0.088
F(000)	352	432	1376
Crystal Size/mm	0.09 x 0.16 x 0.41	0.09 x 0.29 x 0.42	0.13 x 0.20 x 0.39
Temperature/K	120	120	120
Radiation/Å, MoK α	0.71073	0.71073	0.71073
Theta Min-Max/°	3.5, 27.6	3.5, 30.0	2.7, 28.7
Dataset	-11: 10 ; 0: 11 ; 0: 14	-12: 11 ; -12: 12 ; -18: 18	-24: 24 ; -15: 14 ; -19: 23
Tot., Uniq. Data, R(int)	6606, 1987, 0.056	13179, 3090, 0.055	13979, 4234, 0.088
Observed data [I > 2.0 sigma(I)]	1764	2464	3411
Nref, Npar	1764, 109	2304, 136	3137, 218
R, wR2, S	0.0577, 0.4001, 0.84	0.0505, 0.0643, 1.07	0.0664, 0.1024, 0.91
Min. and Max. Resd. Dens./eAng ⁻³	-0.42, 0.49	-0.33, 0.31	-0.50, 0.54

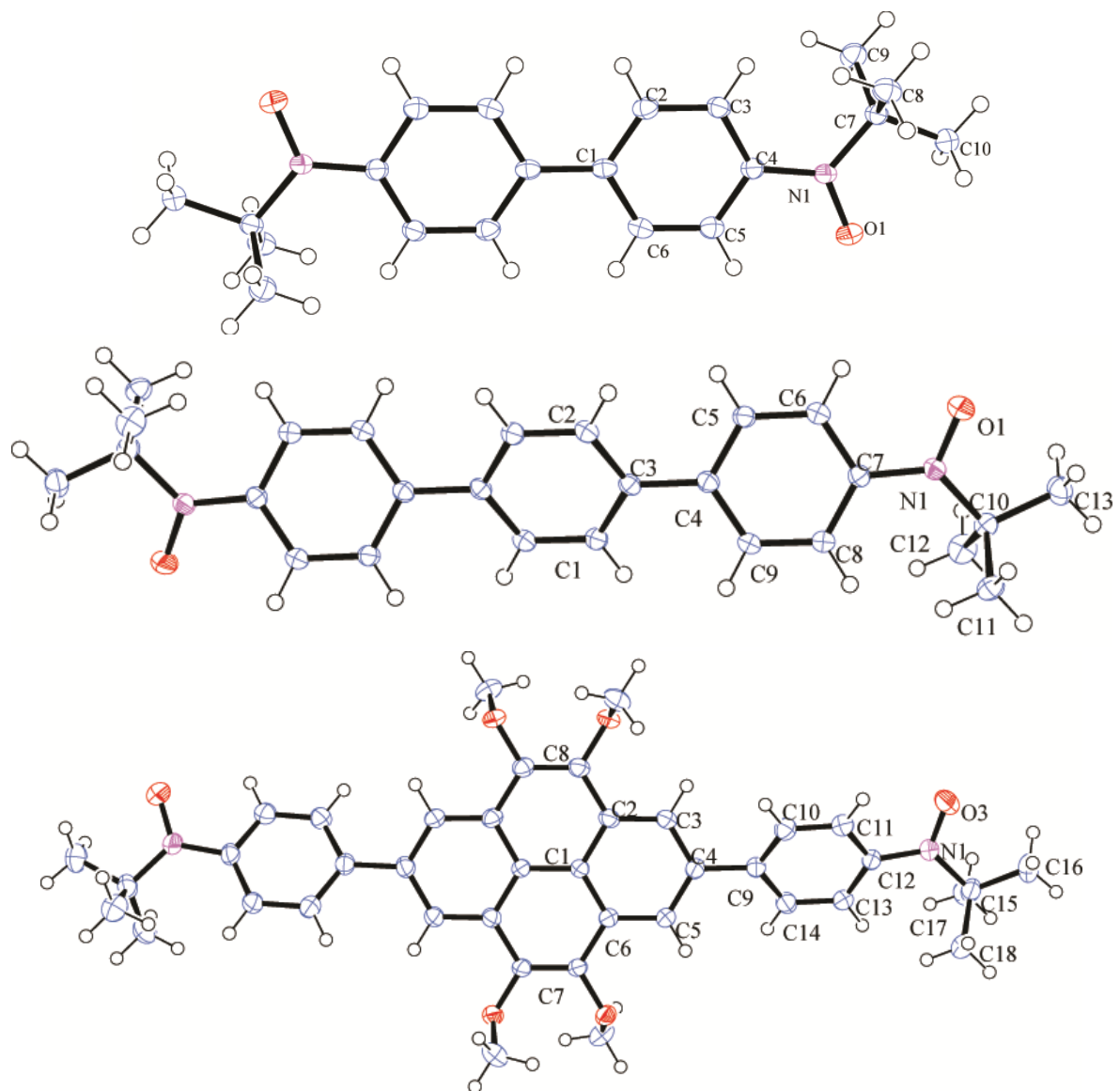


Figure S1: ORTEP diagram, 50 % probability temperature ellipsoid plot.

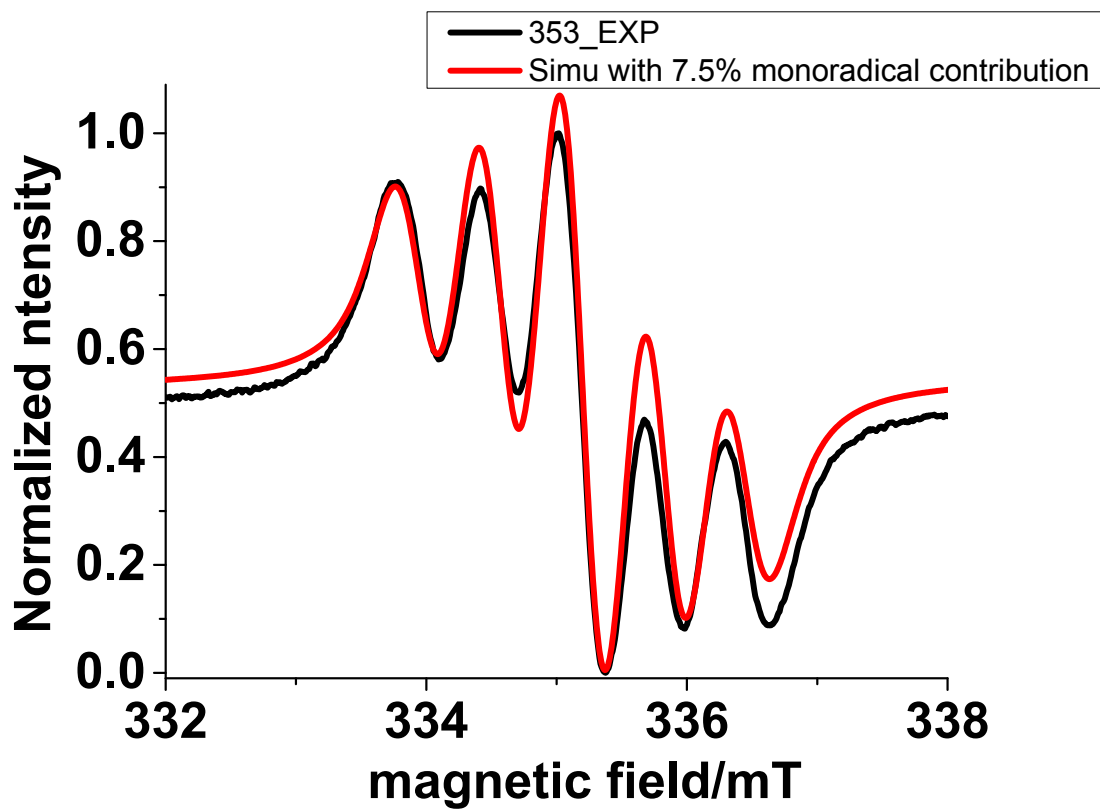


Figure S2: Black: Experimental EPR spectrum of BPNO at 353 K. Red: Simulated spectrum for BPNO with 7.5% contribution from monoradical species.