

Ambient Stable Naphthalenediimide Radical Ions: Synthesis by Solvent-Free, Sonication, Mechanical Grinding or Milling Protocols

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General: All the starting materials were obtained from commercial sources and were used without further purification. The reactions of the synthesis of radical ions were carried out in clear glass sigma vial 4 mL having Inter-Seal™ bonded caps. Thin layer chromatography (TLC) was carried out on aluminium plates coated with silica gel mixed with fluorescent indicator and was sourced from Merck, Germany. MALDI-TOF mass spectrometry data were obtained using a Bruker made Autoflex TOF/TOF instrument with laser repetition rate of 50 psec. 1,8,9-Anthracenetriol was used as the matrix for MALDI-TOF mass spectrometry.

UV-Vis-NIR Spectroscopy: The UV-Vis-NIR absorption spectra were taken using a JASCO V-670 model spectrometer. All UV-Vis spectroscopic experiments except the stability spectra with 0.4 mM were performed in a quartz cuvette with 10.0 mm optical path length. The stability spectra with 0.4 mM concentration were performed using 1.0 mm optical path length quartz cuvette. UV-Grade solvents were used for the spectroscopic experiments. Wavelength reported in nanometres (nm).

EPR: Electron Spin Resonance (ESR) spectra were recorded using Bruker EMX 1444 EPR spectrometer operating at 9.455 GHz. Diphenylpicrylhydrazyl, DPPH ($g = 2.0037$), was used for the calibration of ESR spectrometer. The samples were prepared in dry DCM at 5×10^{-5} under ambient conditions.

FT-IR: Fourier transform infrared (FT-IR) spectra were recorded on Varian 7000 FT-IR spectrometer. Pellets of samples were prepared in a dry, finally ground KBr matrix for data collection. A blank scan was run to cut out the air effects before analysis.

Yield Calculation with the help of UV-Vis-NIR spectroscopy: The UV-Vis-NIR spectroscopic yield of all the compounds were determined by following steps: I) each radical ion was purified by silica-gel column chromatography; II) A calibration curve of the corresponding pure radical ion was plotted by taking the highest absorbance peak (~466 nm) of the UV-Vis spectra with different concentrations in MeCN; III) A solution of the crude product was prepared in MeCN and UV-Vis-NIR spectra was taken in the same solvent, and finally, the resulting spectra was fitted over the calibration curve and on the basis of the crude product concentration the yields were calculated.

General Procedure for Synthesis of Diphosphonium Radical Ions

Method 1- under thermal conditions, with variation of base: A mixture of N,N-disubstituted-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (0.04 mmol), triphenylphosphine (0.16 mmol) and an appropriate base (0.06 mmol) was stirred at the given temperature and time in a vial (clear glass sigma vial 4 mL having Inter-Seal™ bonded caps). The colour of the solution became dark green. The reaction mixture was purified via washing (2-3 times) with hexane-chloroform mixture (4:1) and then the compound was dissolved in CHCl₃ and layered with hexane (CHCl₃/hexane ~ 1:2.5). On slow evaporation under ambient conditions deep-green crystals were obtained within 2-3 days. The obtained crystals were recrystallized to obtain pure radical ions.

Method 2- under thermal conditions using Et₃N as base: A mixture of N,N-disubstituted-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (0.04 mmol), phosphine (0.16 mmol) and Et₃N (0.06 mmol) was stirred at given temperature and time in a vial (clear glass sigma vial 4 mL having Inter-Seal™ bonded caps). The colour of the solution became dark green. The reaction mixture was purified via washing with hexane-chloroform mixture (4:1) for 2-3 times. The solid was further dissolved in CHCl₃ and layered with hexane (CHCl₃/hexane ~ 1:2.5). On slow evaporation under ambient conditions, deep-green crystals were obtained within 2-3 days. The obtained crystals were further recrystallized to obtain pure radical ions.

Method 3- (under thermal conditions using without base): A mixture of N, N-disubstituted-2,6-dibromo- naphthalene-1,4,5,8-tetracarboxylic acid bisimide (0.04 mmol), and phosphines (0.16 mmol) was stirred at given temperature in a vial up to 30 min. The colour of the solution became dark green.

Method 4- (under sonication): A mixture of N, N-disubstituted-2,6-dibromo- naphthalene-1,4,5,8-tetracarboxylic acid bisimide (0.04 mmol), phosphines (0.16 mmol) and Et₃N (0.06 mmol) was sonicated (33 Hz) at room temperature (25 °C) in a vial up to 30 min. The colour of the solution became dark green.

Method 5- (under grinding and ball milling): A mixture of N, N-disubstituted-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (100 mg, 0.16 mmol), triphenylphosphine (265

mg, 1.01 mmol) were taken in mortar pestle and grinded up to 30 min. by adding Et₃N (94 µL, 0.72 mmol) in three parts with 10 min. difference. The mixture became greenish.

Radical ion 1•⁺: N,N-dihexyl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.084 mmol), PPh₃ (88 mg, 0.337 mmol) and Et₃N (18 µl, 0.126 mmol). Yield = 97 %. R_f = 0.5 (CHCl₃/MeOH 8.5: 1.5). M. P. = 205 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for C₆₂H₅₈N₂O₄P₂ [M–Br]^{•+} 956.39, found 956.28. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 3054, 2953, 2856, 1651, 1606, 1516, 1464, 1437. Anal. calcd. for C₆₂H₅₈BrN₂O₄P₂[•]: C, 71.81; H, 5.64; N, 2.70. Anal. found: C, 71.61; H, 5.54; N, 2.63.

Radical ion 2•⁺: N,N-dihexyl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.084 mmol), *p*-OMePPh₃ (119 mg, 0.337 mmol) and Et₃N (17 µl, 0.12 mmol). Yield = 80 %. R_f = 0.5 (CHCl₃/MeOH 9: 1). M. P. = 168 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for C₆₈H₇₀N₂O₁₀P₂ [M–Br]^{•+} 1136.45, found 1136.37. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 2957, 2930, 2859, 1654, 1612, 1594, 1502, 1460. Anal. calcd. for C₆₈H₇₀BrN₂O₁₀P₂[•]: C, 67.10; H, 5.80; N, 2.30. Anal. found: C, 67.03; H, 5.71; N, 2.43.

Radical ion 3•⁺: N,N-dihexyl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.084 mmol), *p*-FPPh₃ (107 mg, 0.337 mmol) and Et₃N (16 µl, 0.12 mmol). Yield = 92 %. R_f = 0.5 (CHCl₃/MeOH 8.5: 1.5). M. P. = 168 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for C₆₂H₅₂F₆N₂O₄P₂ [M–Br]^{•+} 1064.33, found 1064.25. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 2934, 2861, 2740, 2678, 1657, 1596, 1467, 1239, 1164, 1103. Anal. calcd. for C₆₂H₅₂BrF₆N₂O₄P₂[•]: C, 65.04; H, 4.58; N, 2.45. Anal. found: C, 65.30; H, 4.71; N, 2.59.

Radical ion 4•⁺: N,N-dimesityl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.076 mmol), PPh₃ (79 mg, 0.30 mmol) and Et₃N (16 µl, 0.11 mmol). Yield = 93 %. R_f = 0.5 (CHCl₃/MeOH 8.5: 1.5). M. P. = 240 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for C₆₈H₅₄N₂O₄P₂ [M–Br]^{•+} 1024.35, found 1024.30. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 2941, 2863, 1664, 1613, 1439, 1329, 1105, 1029. Anal. calcd. for C₆₈H₅₄BrN₂O₄P₂[•]: C, 73.91; H, 4.93; N, 2.54. Anal. found: C, 73.30; H, 4.78; N, 2.69.

Radical ion 5•⁺: N,N-di(2,6-diisopropylphenyl)-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.067 mmol), PPh₃ (70 mg, 0.269 mmol) and Et₃N (14 µl, 0.10 mmol). Yield = 75 %. R_f = 0.5 (CHCl₃/MeOH 8.5: 1.5). M. P. = 238 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for C₇₄H₆₆N₂O₄P₂ [M–Br]^{•+} 1108.45, found 1108.48. FTIR (KBr

pellet): $\bar{\nu}$ (cm⁻¹) = 2963, 2929, 2865, 1663, 1611, 1441, 1318, 1211, 1104. Anal. calcd. for C₇₄H₆₆BrN₂O₄P₂•: C, 74.74; H, 5.59; N, 2.36. Anal. found: C, 74.09; H, 5.78; N, 2.19.

Radical ion 6•+: N,N-di(2,6-diisopropylphenyl)-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.067 mmol), *p*-FPPh₃ (85 mg, 0.269 mmol) and Et₃N (14 µl, 0.10 mmol). Yield = 70 %. R_f = 0.5 (CHCl₃/MeOH 8.5: 1.5). M. P. = 212 °C. ESI-HRMS: calculated for C₇₄H₆₀F₆N₂O₄P₂ [M–Br]•+ 1216.39, found 1216.39. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 3105, 3076, 2969, 2930, 2870, 1720, 1669, 1593, 1501, 1438, 1331, 1251, 1170, 1058. Anal. calcd. for C₇₄H₆₀BrF₆N₂O₄P₂•: C, 68.52; H, 4.66; N, 2.16. Anal. found: C, 68.18; H, 4.78; N, 2.09.

Radical ion 7•+: N,N-dibenzyl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.083 mmol), PPh₃ (87 mg, 0.332 mmol) and Et₃N (17 µl, 0.12 mmol). Yield = 80 %. R_f = 0.6 (CHCl₃/MeOH 8.5: 1.5). M. P. = 210 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for C₆₄H₄₆N₂O₄P₂ [M–Br]•+ 968.29, found 968.20. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 3059, 1655, 1605, 1462, 1438, 1309, 1210, 1103, 1034. Anal. calcd. for C₆₄H₄₆BrN₂O₄P₂•: C, 73.28; H, 4.42; N, 2.67. Anal. found: C, 72.78; H, 4.78; N, 2.32.

Radical ion 8•+: N,N-di-L-alanine-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.088 mmol), PPh₃ (92 mg, 0.352 mmol) and Et₃N (18 µl, 0.13 mmol). Yield = 90 %. R_f = 0.5 (CHCl₃/MeOH 8.0: 2.0). M. P. = 218 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for C₅₆H₄₂N₂O₈P₂ [M–Br]•+ 932.24, found 932.15. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 3405, 3055, 2937, 1660, 1609, 1462, 1438, 1438, 1312, 1103. Anal. calcd. for C₅₆H₄₂BrN₂O₈P₂•: C, 66.41; H, 4.18; N, 2.77. Anal. found: C, 66.78; H, 4.42; N, 2.39.

Radical ion 9•+: N,N-dibenzyl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.083 mmol), *p*-FPPh₃ (105 mg, 0.332 mmol) and Et₃N (17 µl, 0.12 mmol). Yield = 87 %. R_f = 0.5 (CHCl₃/MeOH 8.5: 1.5). M. P. = 182 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for C₆₄H₄₀F₆N₂O₄P₂ [M–Br]•+ 1076.24, found 1076.10. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 3104, 3068, 3034, 2959, 2929, 2858, 1711, 1661, 1588, 1497, 1452, 1369, 1309, 1247, 1163. Anal. calcd. for C₆₄H₄₀BrF₆N₂O₄P₂•: C, 66.45; H, 3.49; N, 2.42. Anal. found: C, 66.18; H, 3.42; N, 2.28.

Radical ion 10•+: N,N-dimesityl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.076 mmol), *p*-CF₃PPh₃ (140 mg, 0.302 mmol) and Et₃N (16 µl, 0.11 mmol). Yield = 30 %. R_f = 0.6 (CHCl₃/MeOH 8.5: 1.5). M. P. = 234 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for C₇₄H₄₈F₁₈N₂O₄P₂ [M–Br]•+ 1432.28, found 1432.18. FT-IR (KBr

pellet): $\bar{\nu}$ (cm⁻¹) = 3042, 2962, 2925, 2858, 1665, 1610, 1515, 1463, 1325, 1174, 1132, 1063. Anal. calcd. for C₇₄H₄₈BrF₁₈N₂O₄P₂^{•+}: C, 58.74; H, 3.20; N, 1.85. Anal. found: C, 58.68; H, 3.29; N, 2.15.

Radical ion 11^{•+}: N,N-di (*p*-CF₃benzyl)-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.067 mmol), *p*-FPPh₃ (86 mg, 0.270 mmol) and Et₃N (14 μ l, 0.100 mmol). Yield = 70 %. R_f = 0.5 (CHCl₃/MeOH 8.5: 1.5). M. P. = 184 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for C₆₆H₃₈F₁₂N₂O₄P₂ [M–Br]^{•+} 1212.21, found 1212.20. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 3067, 1655, 1611, 1499, 1461, 1310, 1241, 1164. Anal. calcd. for C₆₆H₃₈BrF₁₂N₂O₄P₂^{•+}: C, 61.31; H, 2.96; N, 2.17. Anal. found: C, 61.41; H, 2.29; N, 2.09.

Radical ion 12^{•+}: N,N-dimesityl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.076 mmol), *p*-OMePPh₃ (106 mg, 0.302 mmol) and Et₃N (16 μ l, 0.110 mmol). Yield = 87 %. R_f = 0.6 (CHCl₃/MeOH 8.5: 1.5). M. P. = 252 °C. ESI-HRMS: calculated for C₇₄H₆₆N₂O₁₀P₂ [M–Br]^{•+} 1204.41, found 1204.41. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 3011, 2926, 2839, 2563, 1666, 1618, 1592, 1504, 1457, 1296, 1264, 1184, 1107. Anal. calcd. for C₇₄H₆₆BrN₂O₁₀P₂^{•+}: C, 69.16; H, 5.18; N, 2.18. Anal. found: C, 68.91; H, 5.09; N, 2.37.

Radical ion 13^{•+}: N,N-didodecyl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.066 mmol), PPh₃ (69 mg, 0.264 mmol) and Et₃N (14 μ l, 0.099 mmol). Yield = 90 %. R_f = 0.5 (CHCl₃/MeOH 8.5: 1.5). M. P. = 122 °C. ESI-HRMS: calculated for C₇₄H₈₂N₂O₄P₂ [M–Br]^{•+} 1124.57, found 1124.57. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 2973, 2938, 2739, 2676, 2490, 1665, 1623, 1516, 1460, 1213. Anal. calcd. for C₇₄H₈₂BrN₂O₄P₂^{•+}: C, 73.74; H, 6.86; N, 2.32. Anal. found: C, 73.72; H, 6.69; N, 2.53.

Radical ion 14^{•+}: N,N-dihexyl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.084 mmol), P(n-Bu)₃ (68 mg, 0.337 mmol) and Et₃N (18 μ l, 0.126 mmol). Yield = 90 %. R_f = 0.6 (CHCl₃/MeOH 8.5: 1.5). M. P. = 210 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for C₅₀H₈₂N₂O₄P₂ [M–Br]^{•+} 836.57, found 836.61. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 2960, 2933, 2867, 2676, 1650, 1607, 1461, 1308, 1208. Anal. calcd. for C₅₀H₈₂BrN₂O₄P₂^{•+}: C, 65.49; H, 9.01; N, 3.05. Anal. found: C, 65.52; H, 9.19; N, 3.24.

Radical ion 15^{•+}: N,N-dihexyl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.084 mmol), P(Cyhex)₃ (95 mg, 0.337 mmol) and Et₃N (18 μ l, 0.126 mmol). Yield = 60 %. R_f = 0.5 (CHCl₃/MeOH 9.0: 1.0). M. P. = 194 °C. MS (MALDI-TOF matrix: 1,8,9-

Anthracenetriol): calculated for $C_{62}H_{94}N_2O_4P_2$ [M–Br] $^{•+}$ 992.67, found 992.58. FT-IR (KBr pellet): $\bar{\nu}$ (cm^{-1}) = 2931, 2857, 2678, 1657, 1615, 1459, 1307, 1208, 1029. Anal. calcd. for $C_{62}H_{94}BrN_2O_4P_2^{•+}$: C, 69.38; H, 8.83; N, 2.61. Anal. found: C, 69.12; H, 8.79; N, 2.80.

Radical ion 16 $^{•+}$: N,N-didodecyl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.066 mmol), P(Cyhex)₃ (74 mg, 0.264 mmol) and Et₃N (14 μl , 0.099 mmol). Yield = 67 %. R_f = 0.6 (CHCl₃/MeOH 8.0: 1.0). M. P. = 200 °C. ESI-HRMS: calculated for $C_{74}H_{118}N_2O_4P_2$ [M–Br] $^{•+}$ 1160.85, found 1160.73. FT-IR (KBr pellet): $\bar{\nu}$ (cm^{-1}) = 2928, 2854, 2679, 2490, 1723, 1658, 1620, 1519, 1461, 1398. Anal. calcd. for $C_{74}H_{118}BrN_2O_4P_2^{•+}$: C, 71.58; H, 9.58; N, 2.26. Anal. found: C, 71.43; H, 9.41; N, 2.10.

Radical ion 17 $^{•+}$: N,N-dimesityl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.076 mmol), P(Cyhex)₃ (85 mg, 0.302 mmol) and Et₃N (16 μl , 0.110 mmol). Yield = 60 %. R_f = 0.5 (CHCl₃/MeOH 8.0: 1.0). M. P. = 260 °C. ESI-HRMS: calculated for $C_{68}H_{90}N_2O_4P_2$ [M–Br] $^{•+}$ 1060.64, found 1060.53. FT-IR (KBr pellet): $\bar{\nu}$ (cm^{-1}) = 2934, 2856, 2740, 2678, 2491, 1720, 1676, 1621, 1592, 1519, 1466, 1444, 1300, 1230. Anal. calcd. for $C_{68}H_{90}BrN_2O_4P_2^{•+}$: C, 71.56; H, 7.95; N, 2.45. Anal. found: C, 71.47; H, 7.91; N, 2.32.

Radical ion 18 $^{•+}$: N,N-dibenzyl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.083 mmol), PEt₃ (39 mg, 0.332 mmol) and Et₃N (17 μl , 0.12 mmol). Yield = 95 %. R_f = 0.5 (CHCl₃/MeOH 8.5: 1.5). M. P. = 183 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for $C_{40}H_{46}N_2O_4P_2$ [M–Br] $^{•+}$ 680.29, found 680.16. FT-IR (KBr pellet): $\bar{\nu}$ (cm^{-1}) = 2974, 2939, 2740, 2677, 2490, 1647, 1614, 1515, 1457, 1307, 1212, 1045. Anal. calcd. for $C_{40}H_{46}BrN_2O_4P_2^{•+}$: C, 63.16; H, 6.10; N, 3.68. Anal. found: C, 63.27; H, 5.99; N, 3.79.

Radical ion 19 $^{•+}$: N,N-di (*p*-CF₃benzyl)-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.067 mmol), PEt₃ (32 mg, 0.270 mmol) and Et₃N (14 μl , 0.100 mmol). Yield = 65 %. R_f = 0.5 (CHCl₃/MeOH 8.5: 1.5). M. P. = 215 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for $C_{42}H_{44}F_6N_2O_4P_2$ [M–Br] $^{•+}$ 816.27, found 816.34. FT-IR (KBr pellet): $\bar{\nu}$ (cm^{-1}) = 2976, 2912, 1665, 1642, 1617, 1459, 1325, 1164, 1120. Anal. calcd. for $C_{42}H_{44}BrF_6N_2O_4P_2^{•+}$: C, 56.26; H, 4.95; N, 3.12. Anal. found: C, 56.27; H, 4.91; N, 3.20.

Radical ion 20 $^{•+}$: N,N-dimesityl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.076 mmol), PEt₃ (36 mg, 0.302 mmol) and Et₃N (16 μl , 0.110 mmol). Yield = 93 %. R_f =

0.5 (CHCl₃/MeOH 8.5: 1.5). M. P. = 225 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for C₄₄H₅₄N₂O₄P₂ [M–Br]^{•+} 736.35, found 736.31. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 2974, 2936, 2737, 2678, 2490, 1665, 1621, 1516, 1458, 1212, 1041. Anal. calcd. for C₄₄H₅₄BrN₂O₄P₂[•]: C, 64.70; H, 6.66; N, 3.43. Anal. found: C, 64.61; H, 6.51; N, 3.34.

Radical ion 21^{•+}: N,N-didodecyl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.066 mmol), P(n-Oct)₃ (98 mg, 0.264 mmol) and Et₃N (14 µl, 0.099 mmol). Yield = 70 %. R_f = 0.6 (CHCl₃/MeOH 8.0: 1.0). M. P. = 95 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for C₈₆H₁₅₄N₂O₄P₂ [M–Br]^{•+} 1341.14, found 1341.28. FT-IR (could not observed due to sticky nature). Anal. calcd. for C₈₆H₁₅₄BrN₂O₄P₂[•]: C, 72.64; H, 10.92; N, 1.97. Anal. found: C, 72.61; H, 10.53; N, 2.02.

Radical ion 22^{•+}: N,N-dihexyl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.084 mmol), P(n-Oct)₃ (125 mg, 0.337 mmol) and Et₃N (18 µl, 0.126 mmol). Yield = 70 %. R_f = 0.6 (CHCl₃/MeOH 8.0: 1.0). M. P. = 122 °C. ESI-HRMS: calculated for C₇₄H₁₃₀N₂O₄P₂ [M–Br]^{•+} 1172.95, found 1172.95. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 2931, 2857, 2678, 1657, 1615, 1459, 1307, 1208, 1029. Anal. calcd. for C₇₄H₁₃₀BrN₂O₄P₂[•]: C, 70.89; H, 10.45; N, 2.23. Anal. found: C, 70.77; H, 10.33; N, 2.32.

Radical ion 23^{•+}: N,N-dihexyl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.083 mmol), PMe₃ (25 mg, 0.332 mmol) and Et₃N (17 µl, 0.12 mmol). Yield = 83 %. R_f = 0.6 (CHCl₃/MeOH 8.0: 2.0). M. P. = 144 °C. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): calculated for C₃₂H₄₆N₂O₄P₂ [M–Br]^{•+} 584.29, found 584.51. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 2957, 2931, 2876, 2490, 1704, 1661, 1615, 1517, 1460, 1310, 1210, 1098. Anal. calcd. for C₃₂H₄₆BrN₂O₄P₂[•]: C, 57.83; H, 6.98; N, 4.22. Anal. found: C, 57.78; H, 6.91; N, 4.17.

Radical ion 24^{•+}: N,N-di (*p*-CF₃benzyl)-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (50 mg, 0.067 mmol), P(n-Oct)₃ (100 mg, 0.270 mmol) and Et₃N (14 µl, 0.100 mmol). Yield = 60 %. R_f = 0.5 (CHCl₃/MeOH 8.0: 1.0). M. P. = 180 °C. ESI-HRMS: calculated for C₇₈H₁₁₆F₆N₂O₄P₂ [M–Br]^{•+} 1320.83, found 1320.83. FT-IR (KBr pellet): $\bar{\nu}$ (cm⁻¹) = 2930, 2856, 2677, 1657, 1615, 1519, 1463, 1327, 1212, 1163, 1125. Anal. calcd. for C₇₈H₁₁₆BrF₆N₂O₄P₂[•]: C, 66.84; H, 8.34; N, 2.00. Anal. found: C, 67.00; H, 8.21; N, 1.82.

Synthesis of 25⁺: A mixture of N,N-dihexyl-2,6-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (300 mg, 0.50 mmol), triphenylphosphine (393 mg, 1.5 mmol) and Pd (OAc)₂ (6.0 mg,

0.02 mmol) in dry 30 mL toluene was heated to reflux for 3 h. The reaction was cooled and toluene was evaporated under vacuum and the crude product was dissolved in CHCl_3 and purified by silica-gel column chromatography (100-200 mesh) with $\text{CHCl}_3/\text{MeOH}$ as eluent. Yield = 70 %. R_f = 0.6 (9:1; $\text{CHCl}_3/\text{MeOH}$). M. P.: 140 °C. ^1H NMR (500 MHz, CDCl_3 , 298 K, TMS): δ (ppm) = 8.91 (broad, 2H), 8.37 (d, J = 14.5, 1H), 7.81-7.78 (m, 9H, PPh_3), 7.72-7.68 (m, 6H, PPh_3), 4.09 (t, J = 7.0, 2H NCH_2), 3.85 (t, J = 7.0, 2H NCH_2), 1.38-1.04 (m, 16H, CH_2), 0.87 (t, J = 7.0, 3H, CH_3), 0.82 (t, J = 7.0, 3H, CH_3). ^{31}P (202 MHz, CDCl_3 , 298 K, H_3PO_4): δ (ppm) = 30.72. MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): Calculated for $\text{C}_{44}\text{H}_{44}\text{N}_2\text{O}_4\text{P} [\text{M}-\text{Br}]^+$ 695.30, found 695.40. Anal. calcd. for $\text{C}_{44}\text{H}_{44}\text{BrN}_2\text{O}_4\text{P}$: C, 68.13; H, 5.72; N, 3.61. Anal. found: C, 68.09; H, 5.67; N, 3.67.

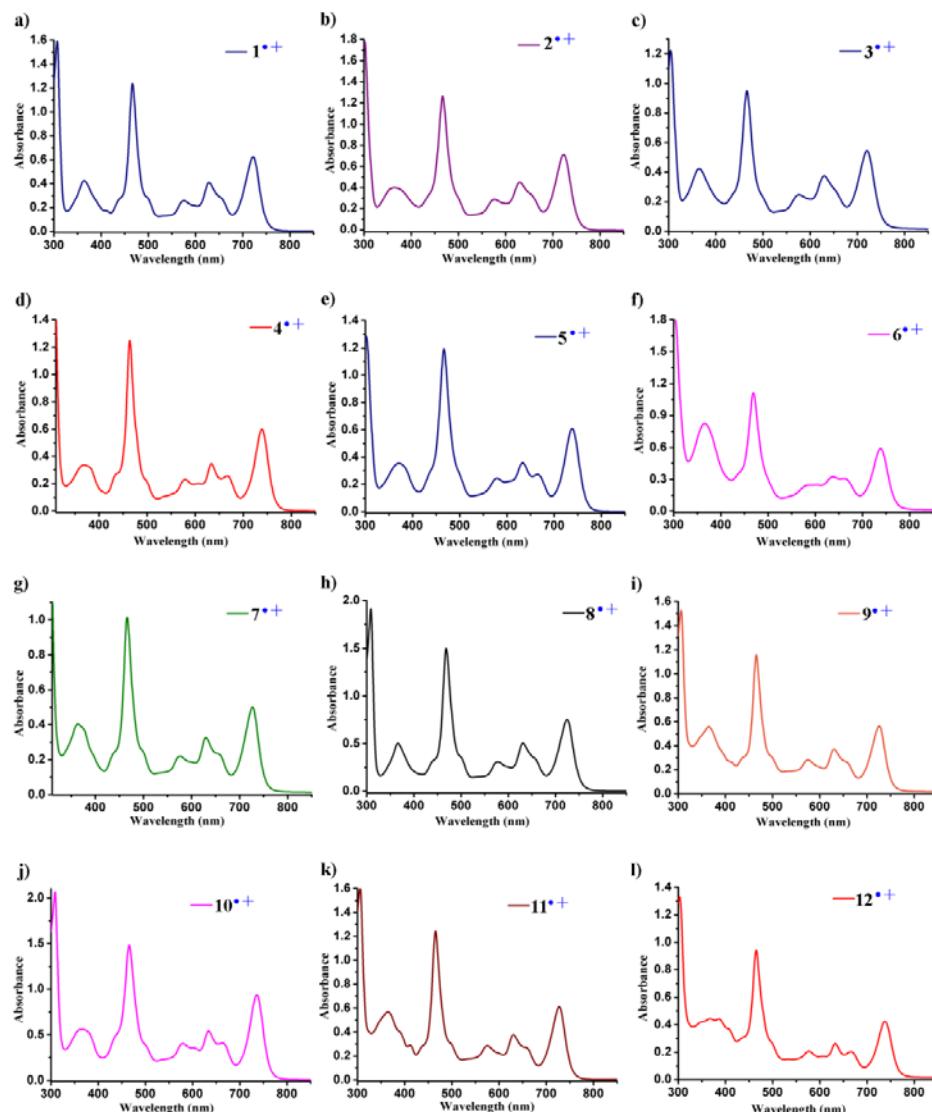


Figure S1: UV-Vis-NIR spectra of the synthesized radical ions **1 \bullet +**-**12 \bullet +** in MeCN at 5×10^{-5} M.

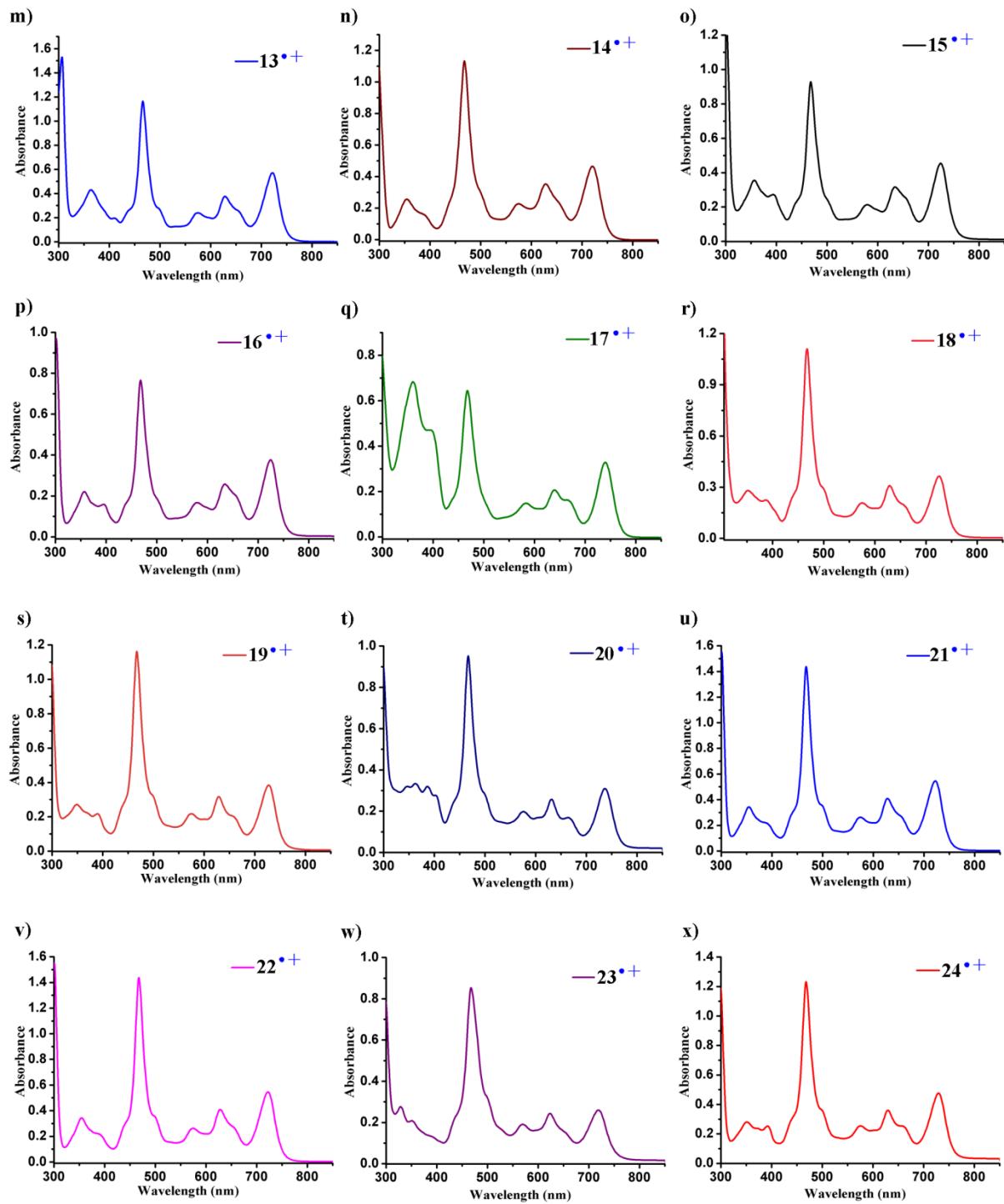


Figure S2: UV-Vis-NIR spectra of the synthesized radical ions $13^{\bullet+}$ - $24^{\bullet+}$ in MeCN at 5×10^{-5} M.

Table S1: UV-Vis absorption characteristics of compound **1^{•+}-24^{•+}**.

Compound	$\lambda_{\text{abs}}/\text{nm} (\epsilon/\text{mol}^{-1} \text{cm}^{-1})$
1^{•+}	466 (24590), 573 (4855), 628 (7901), 722 (12100)
2^{•+}	467 (25309), 576 (5735), 630 (8963), 723 (14242)
3^{•+}	466 (19007), 576 (4954), 630 (7498), 720 (10857)
4^{•+}	466 (24686), 577 (5780), 633 (7324), 662 (5600), 735 (12446)
5^{•+}	467 (23875), 579 (4894), 633 (7169), 665 (5454), 738 (12197)
6^{•+}	469 (22260), 637 (6475), 664 (6115), 739 (11800)
7^{•+}	466 (20312), 576 (4401), 630 (6516), 659 (4582), 727 (10003)
8^{•+}	468 (29998), 578 (6173), 631 (10057), 725 (15038)
9^{•+}	466 (23075), 575 (5635), 630 (7444), 726 (11301)
10^{•+}	466 (29675), 579 (8058), 634 (10851), 663 (8188), 736 (18776)
11^{•+}	465 (24947), 579 (5593), 630 (7573), 727 (12206)
12^{•+}	465 (18879), 577 (4126), 633 (5229), 666 (4088), 738 (8484)
13^{•+}	466 (23296), 575 (4791), 628 (7525), 722 (11434)
14^{•+}	468 (22673), 575 (4536), 629 (7038), 721 (9289)
15^{•+}	467 (18481), 579 (4272), 634 (6330), 724 (9093)
16^{•+}	468 (15320), 580 (3335), 634 (5144), 725 (7502)
17^{•+}	468 (13000), 584 (3015), 640 (4180), 663 (3298), 739 (6623)
18^{•+}	467 (22231), 575 (4146), 629 (6174), 725 (7278)
19^{•+}	467 (23248), 575 (4355), 629 (6337), 727 (7681)
20^{•+}	467 (19052), 576 (3958), 631 (5144), 666 (3354), 737 (6180)
21^{•+}	468 (28751), 575 (5250), 628 (8174), 722 (10927)
22^{•+}	468 (28500), 575 (5160), 628 (8097), 723 (10870)
23^{•+}	468 (17074), 570 (3818), 623 (4877), 719 (5196)
24^{•+}	468 (24661), 576 (5073), 629 (7180), 729 (9518)

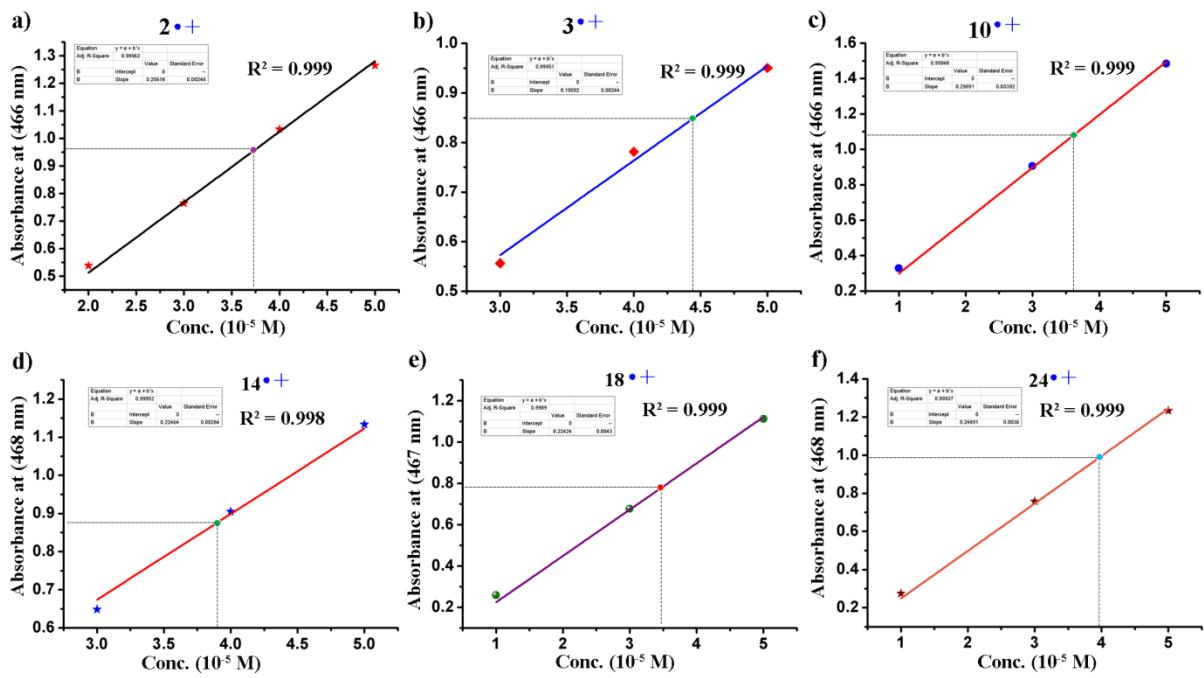


Figure S3: Representative calibration curve from UV-Vis-NIR absorption spectroscopy: a) $2\cdot^+$; b) $3\cdot^+$; c) $10\cdot^+$; d) $14\cdot^+$; e) $18\cdot^+$; f) $24\cdot^+$ in MeCN.

Yield Calculation method; step wise: (i) The crude product was dried in vacuum and stock solution was made by dissolving ~5.0 mg of crude produced in 1.0 mL of MeCN solvent. (ii) ~25 μ L of stock solution was taken in a cuvette having 2975 μ L MeCN. (iii) The UV-Vis spectra was taken and fitted over calibration curve. (iv) on the basis of absorbance at 466 nm the concentration of the cuvette solution was determined. (v) on that basis the concentration of the stock solution was determined. (vi) and so the weight of radical ion required for formation of that particular molar concentration was determined. Finally, on the basis of mg of pure compounds present in 5.0 mg of crude product, the total weight of formation of the radical ion in the reaction was calculated and the percentage yield was determined.

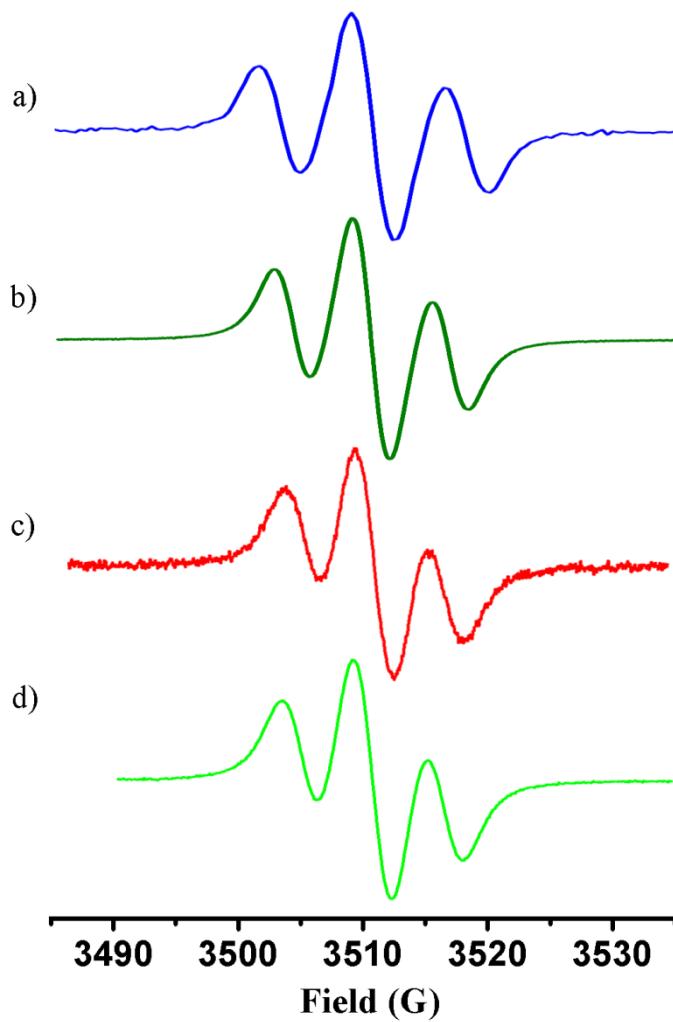


Figure S4: Solution state X-band EPR spectra of representative radical ions: a) **1^{•+}**; b) **2^{•+}**; c) **19^{•+}** and d) **23^{•+}**. Conditions; 5×10^{-4} M in DCM. The g values for all the three lines are as follows:

1^{•+}: g = 2.0079, 2.0043 and 2.0007.

2^{•+}: g = 2.0069, 2.0044 and 2.0051.

19^{•+}: g = 2.0074, 2.0043 and 2.0037.

23^{•+}: g = 2.0067, 2.0045 and 2.0007.

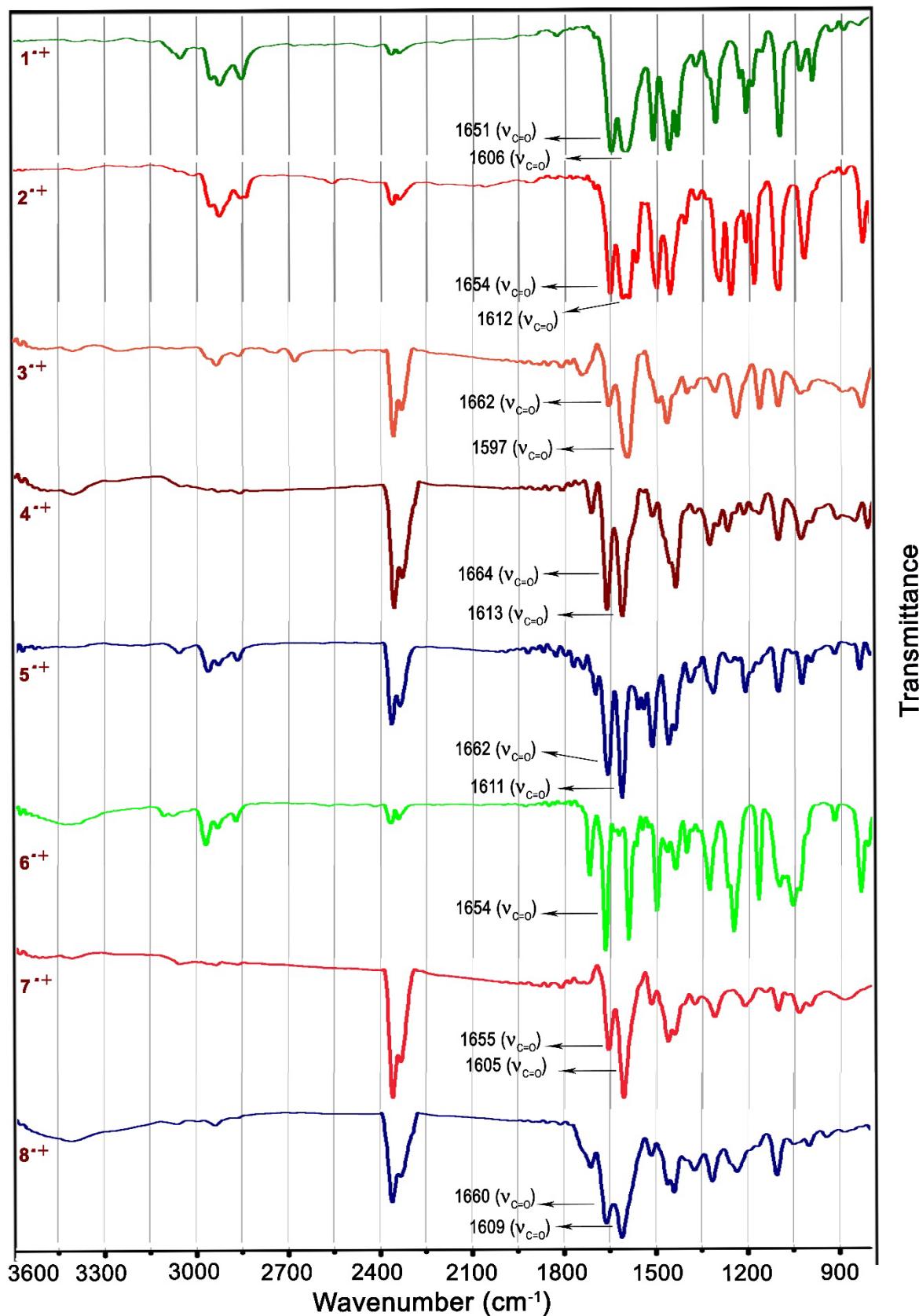


Figure S5: FT-IR spectra of radical ions **1•+**-**8•+**.

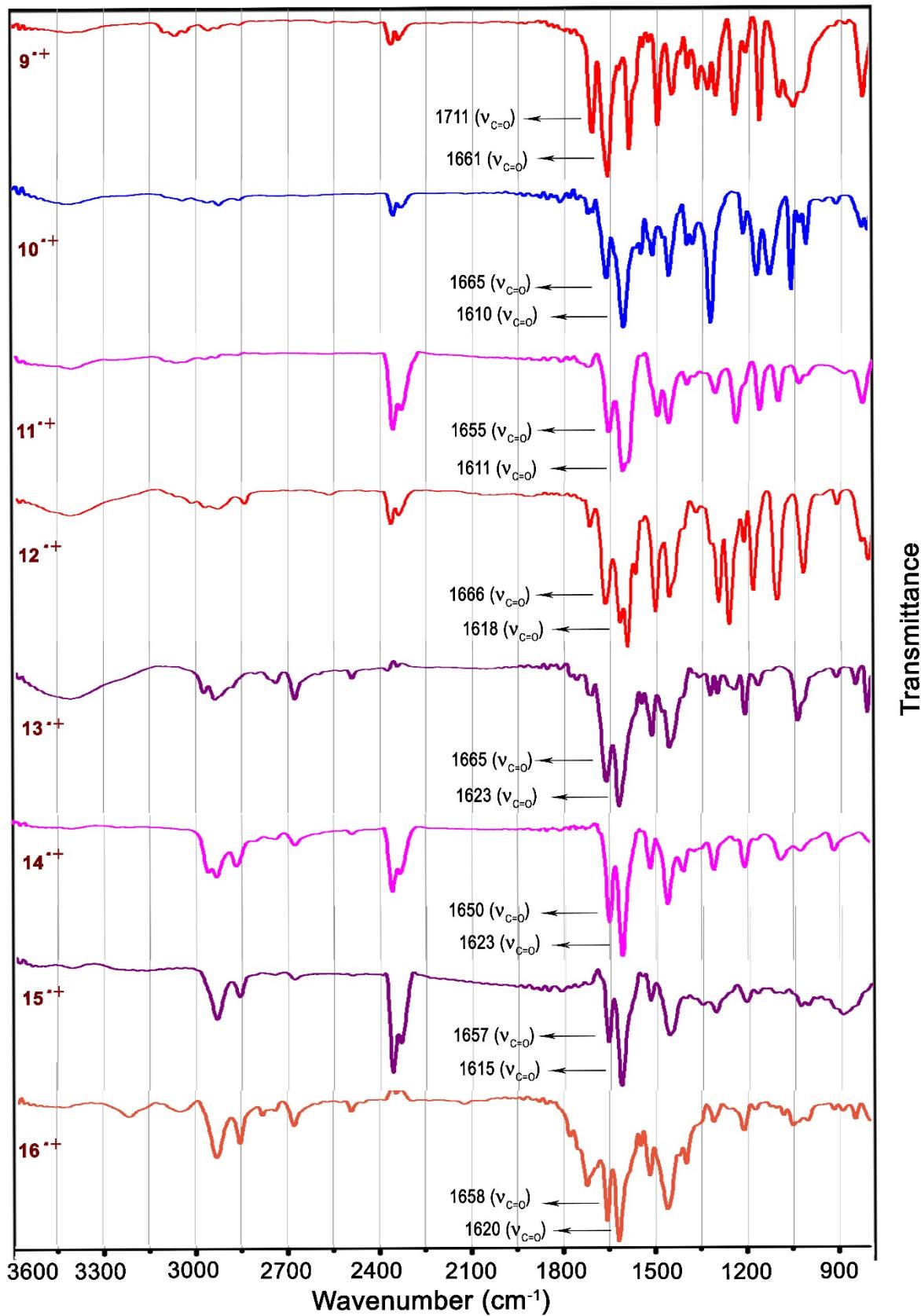


Figure S6: FT-IR spectra of radical ions $9^{\bullet+}$ - $16^{\bullet+}$.

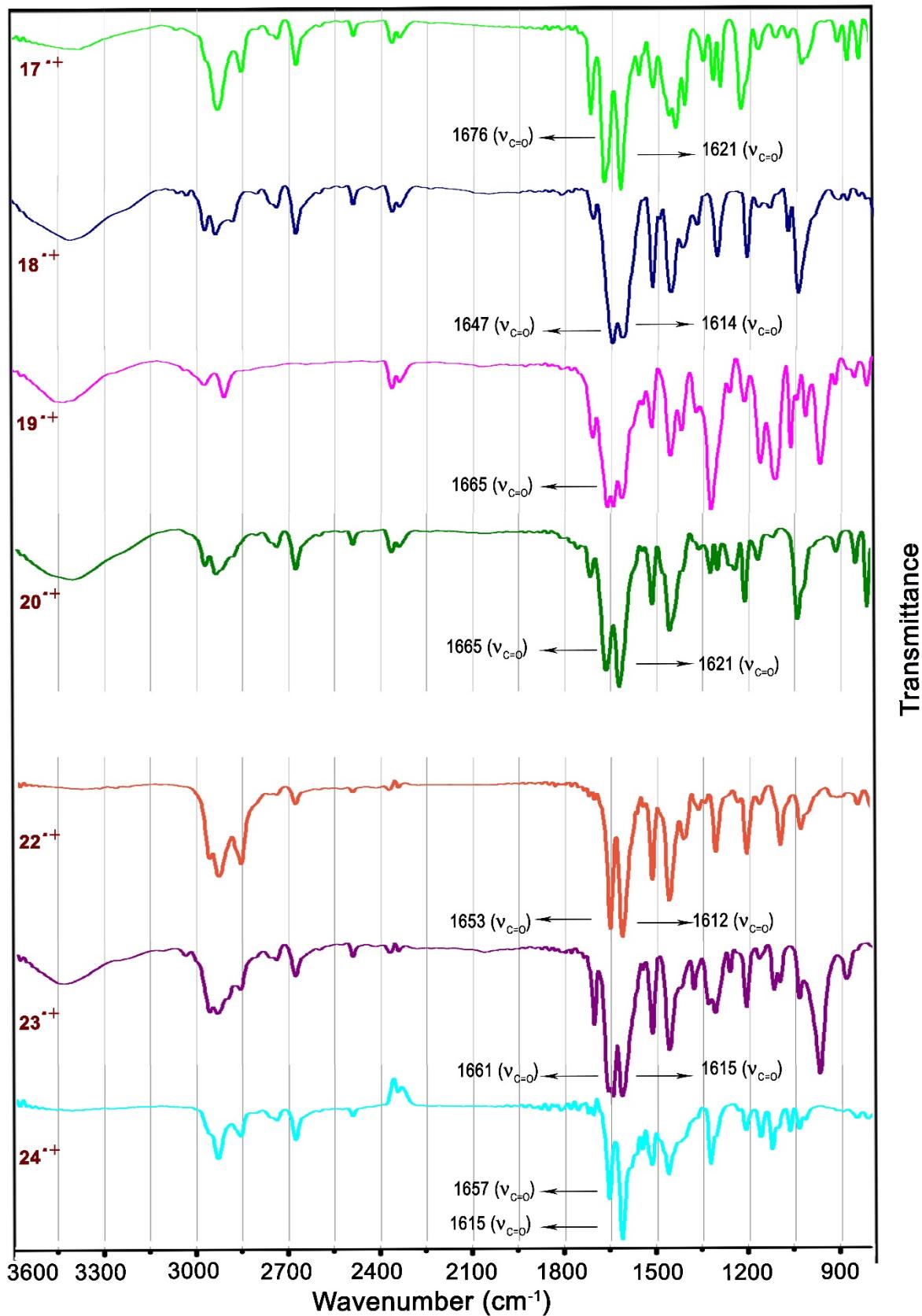


Figure S7: FT-IR spectra of radical ions $17\cdot^+$ - $24\cdot^+$.

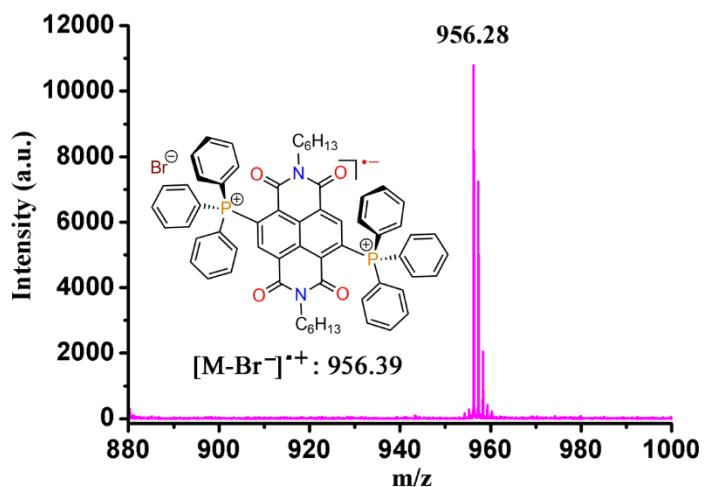


Figure S8: MALDI-TOF mass spectrometry of molecule **1^{•+}**.

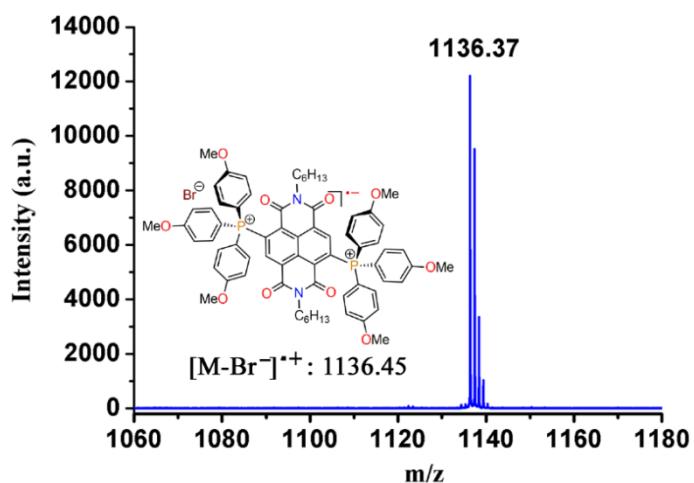


Figure S9: MALDI-TOF mass spectrometry of molecule **2^{•+}**.

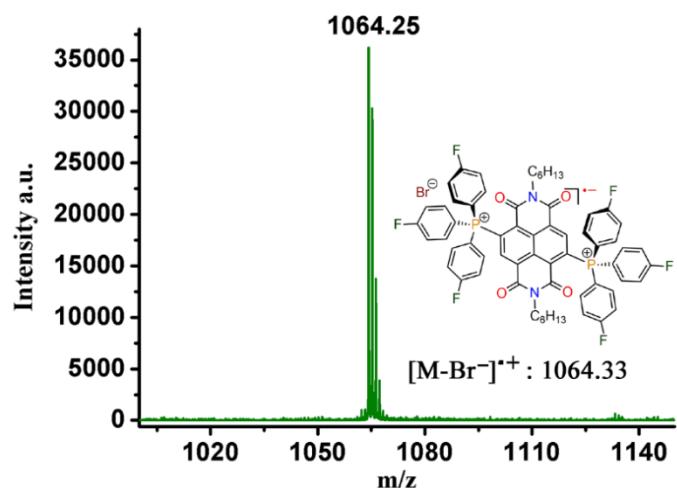


Figure S10: MALDI-TOF mass spectrometry of molecule **3^{•+}**.

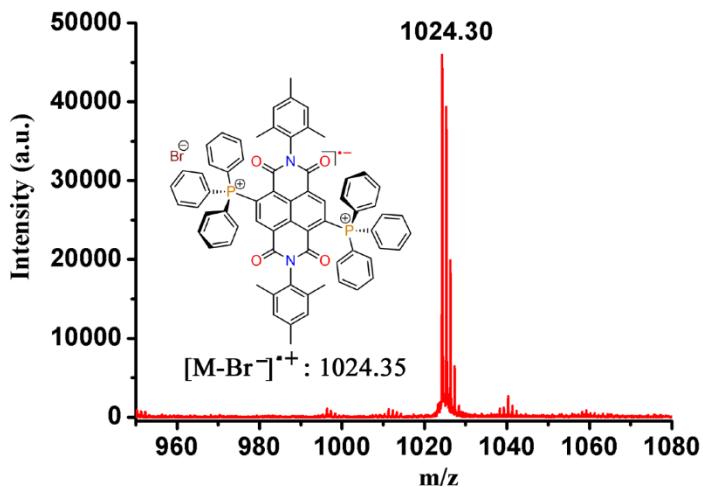


Figure S11: MALDI-TOF mass spectrometry of molecule **4^{•+}**.

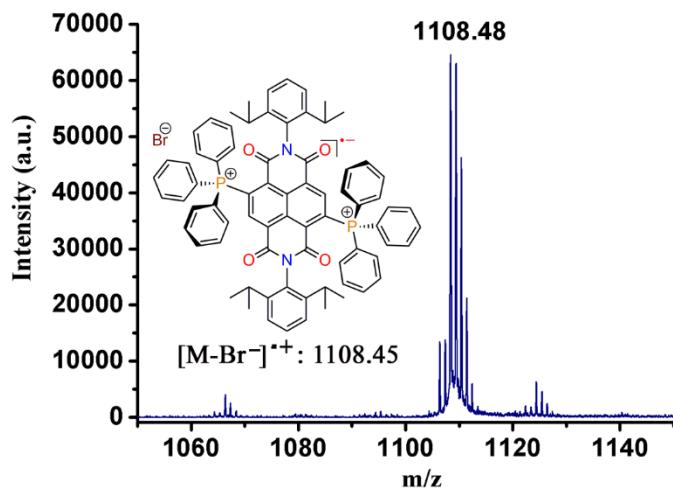


Figure S12: MALDI-TOF mass spectrometry of molecule **5^{•+}**.

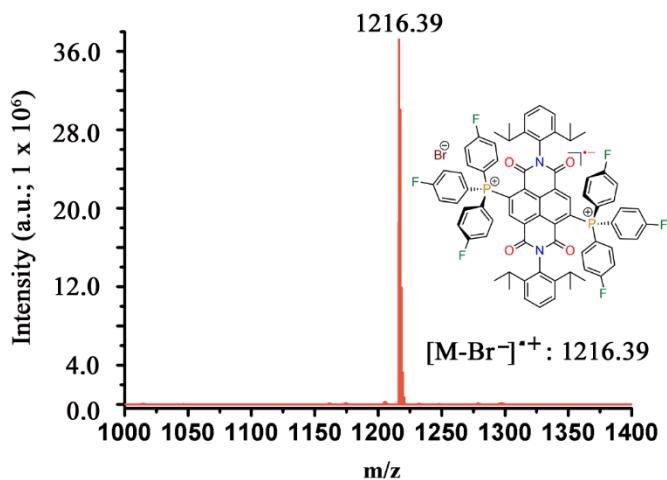


Figure S13: ESI-HRMS mass spectrometry of molecule **6^{•+}**.

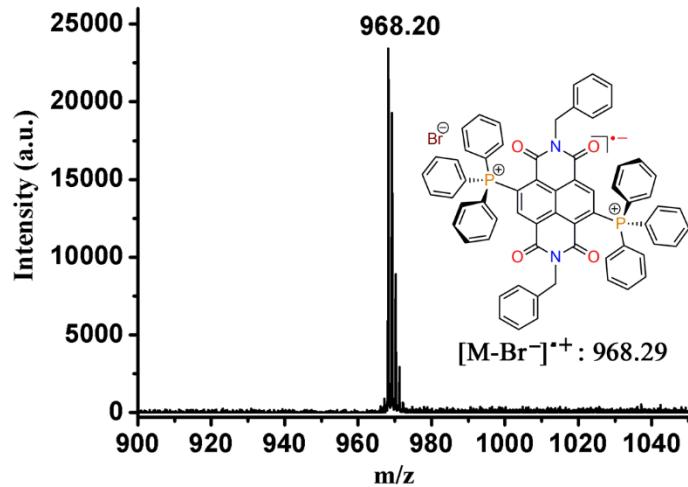


Figure S14: MALDI-TOF mass spectrometry of molecule $7^{\bullet+}$.

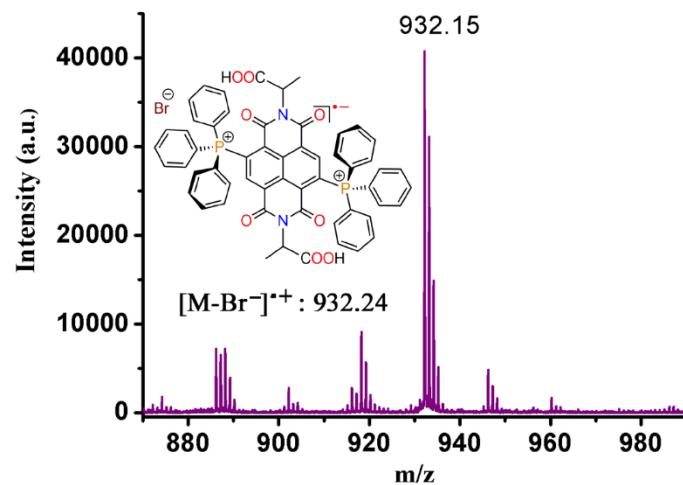


Figure S15: MALDI-TOF mass spectrometry of molecule $8^{\bullet+}$.

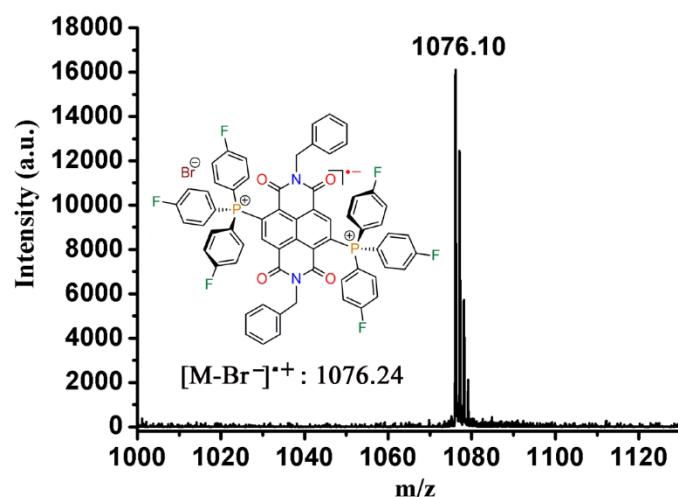


Figure S16: MALDI-TOF mass spectrometry of molecule $9^{\bullet+}$.

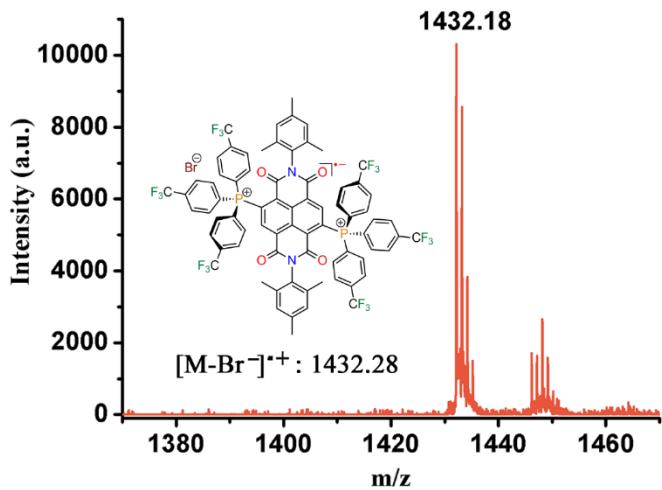


Figure S17: MALDI-TOF mass spectrometry of molecule **10^{•+}**.

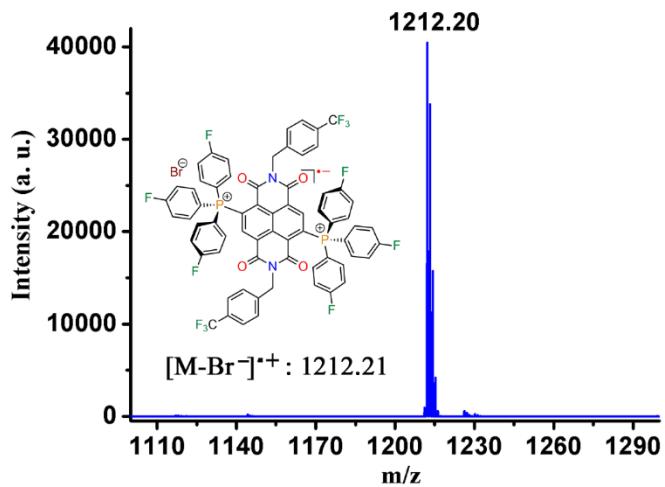


Figure S18: MALDI-TOF mass spectrometry of molecule **11^{•+}**.

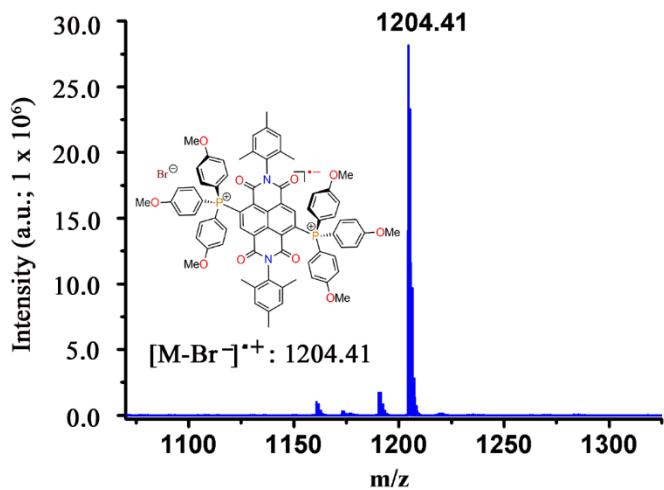


Figure S19: ESI-HRMS mass spectrometry of molecule **12^{•+}**.

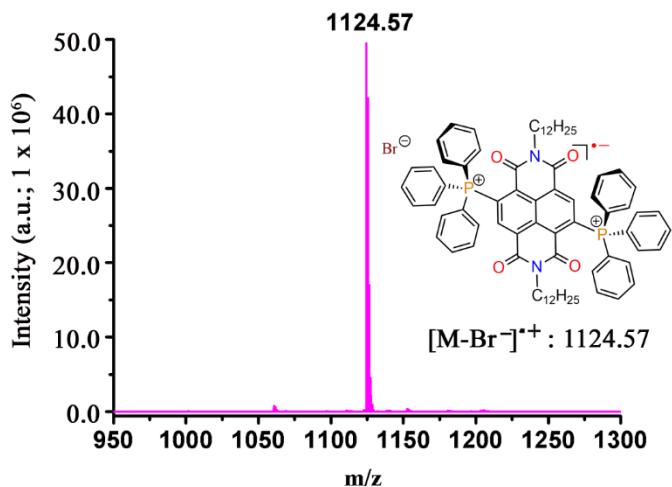


Figure S20: ESI-HRMS mass spectrometry of molecule **13^{•+}**.

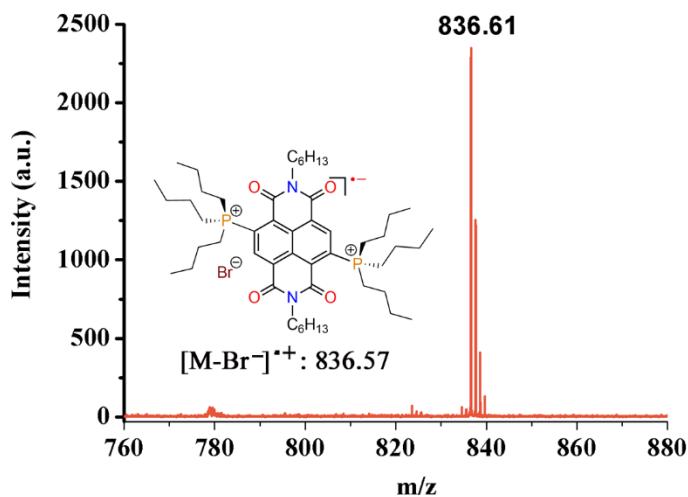


Figure S21: MALDI-TOF mass spectrometry of molecule **14^{•+}**.

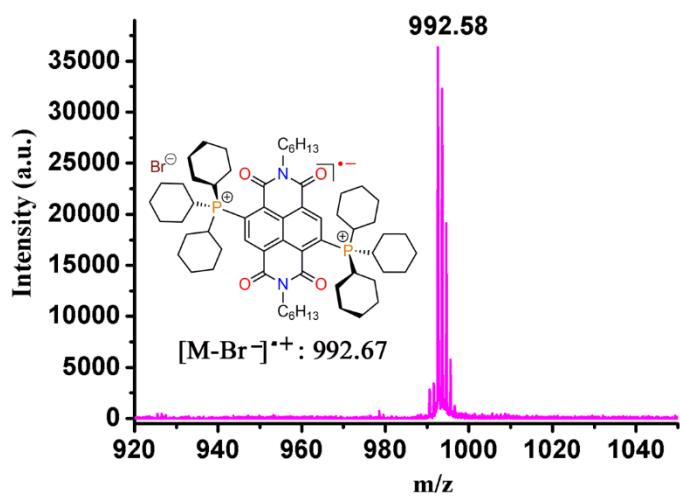


Figure S22: MALDI-TOF mass spectrometry of molecule **15^{•+}**.

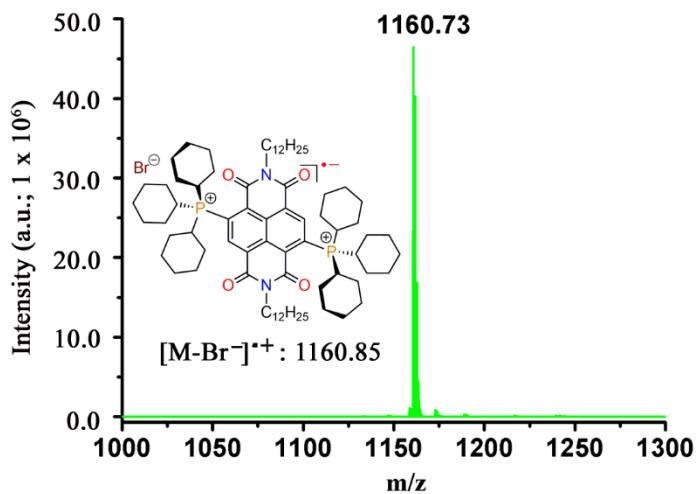


Figure S23: ESI-HRMS mass spectrometry of molecule **2B.16 $•^+$** .

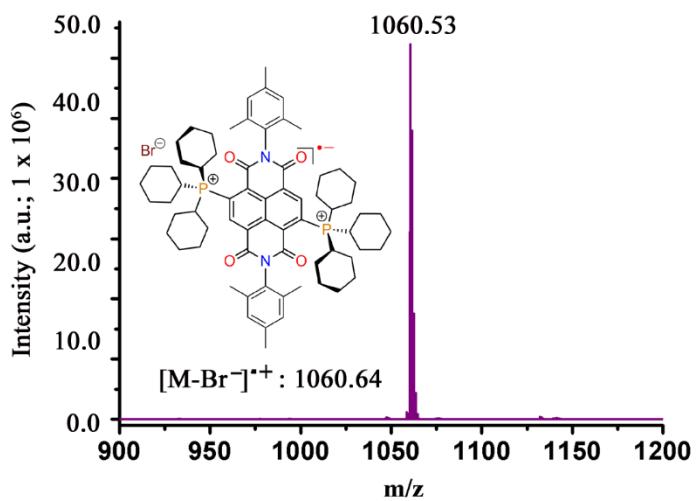


Figure S24: ESI-HRMS mass spectrometry of molecule **17 $•^+$** .

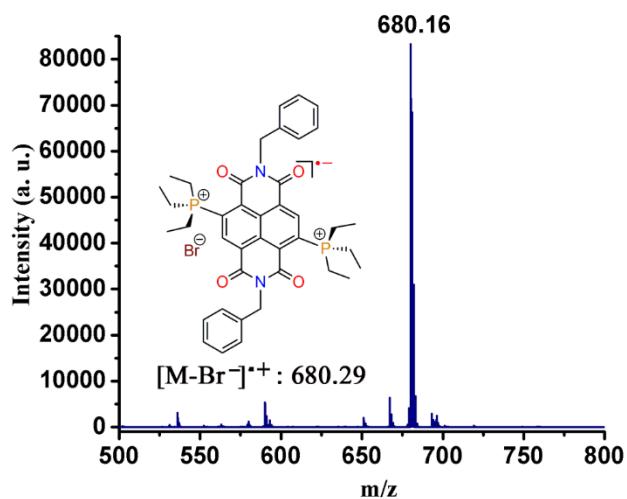


Figure S25: MALDI-TOF mass spectrometry of molecule **18 $•^+$** .

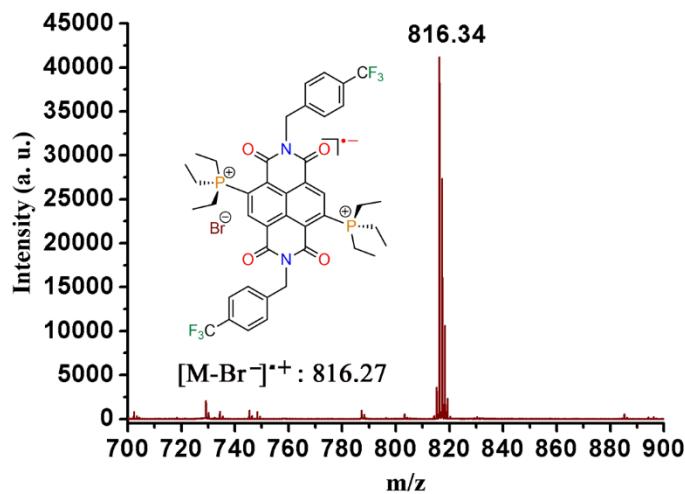


Figure S26: MALDI-TOF mass spectrometry of molecule $\mathbf{19}^{\bullet+}$.

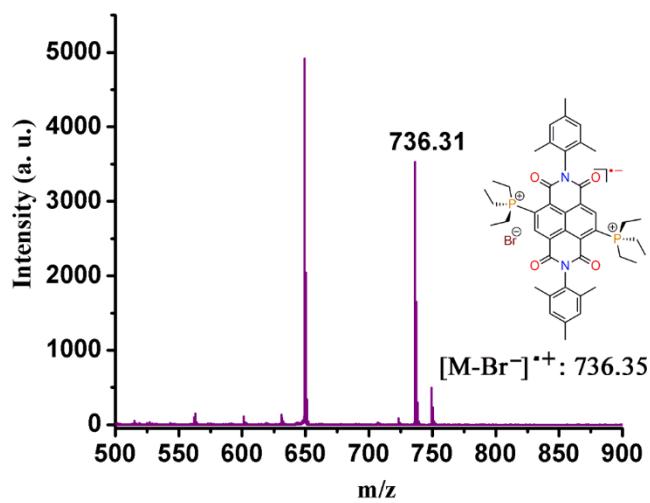


Figure S27: MALDI-TOF mass spectrometry of molecule $\mathbf{20}^{\bullet+}$.

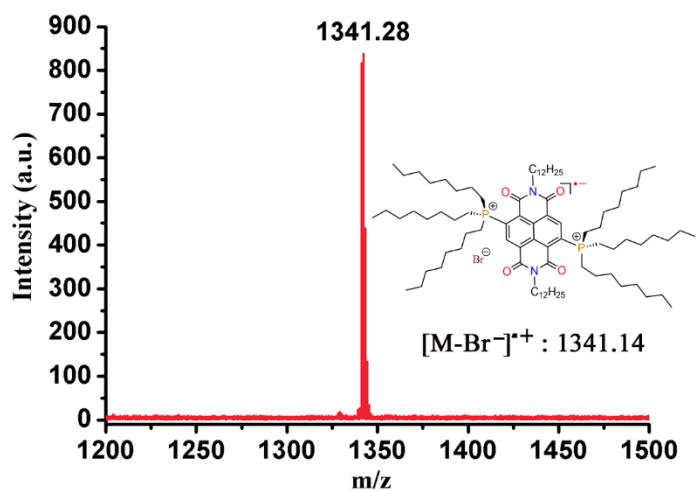


Figure S28: MALDI-TOF mass spectrometry of molecule $\mathbf{21}^{\bullet+}$.

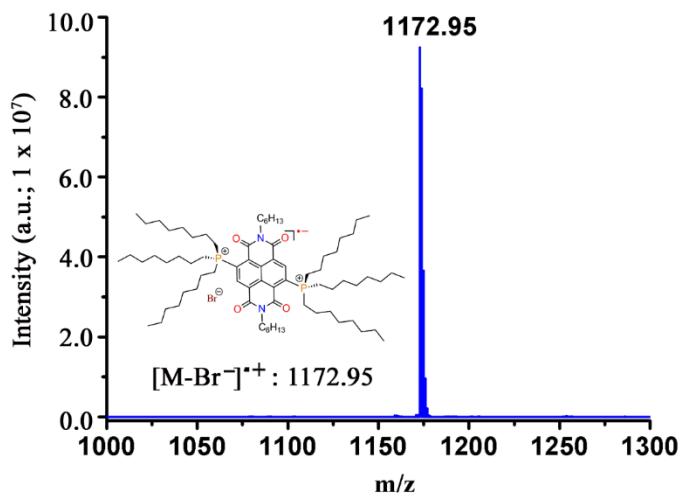


Figure S29: ESI-HRMS mass spectrometry of molecule $22^{\bullet+}$.

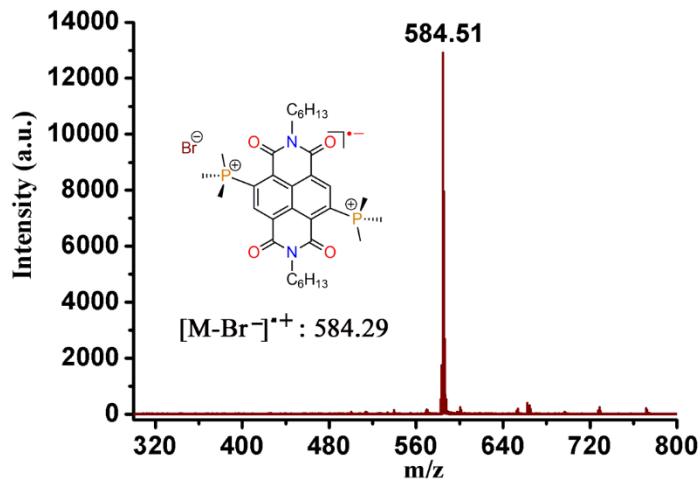


Figure S30: MALDI-TOF mass spectrometry of molecule $23^{\bullet+}$.

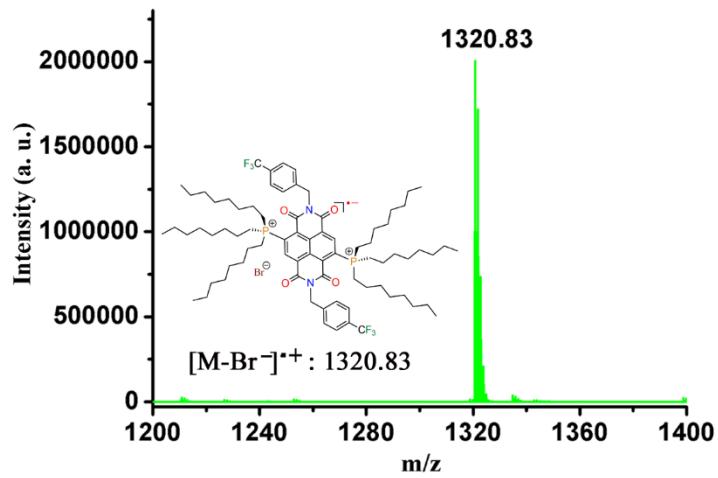


Figure S31: ESI-HRMS mass spectrometry of molecule $24^{\bullet+}$.

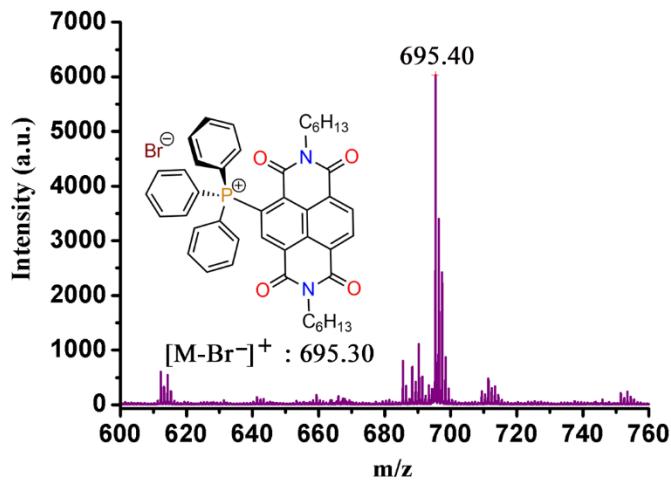


Figure S32: MALDI-TOF mass spectrometry of molecule 25^+ .

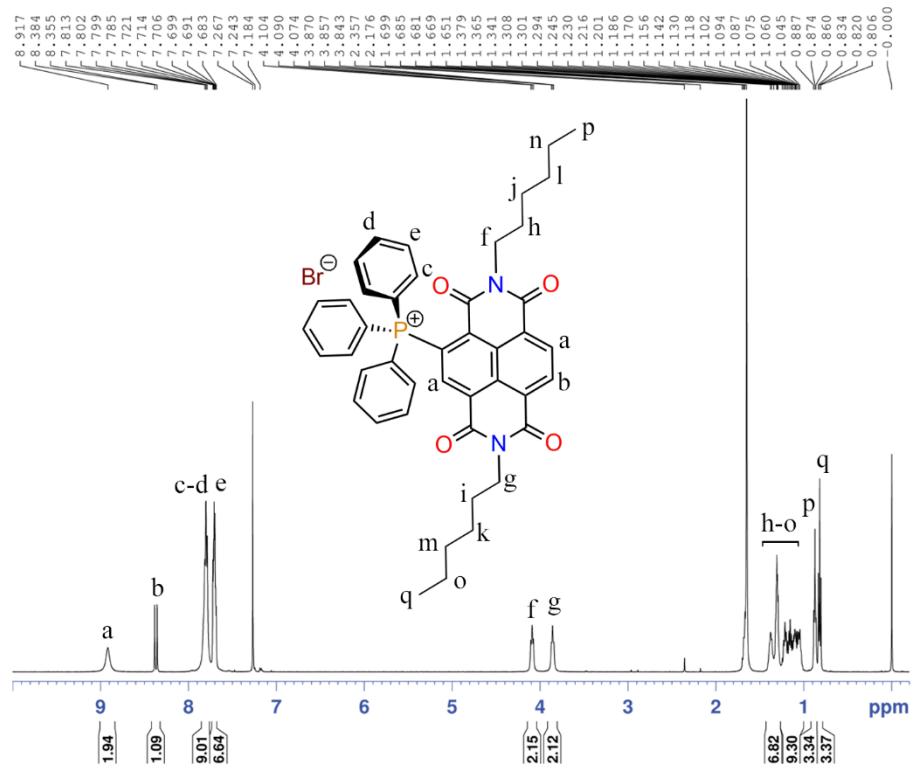


Figure S33: 500 MHz ${}^1\text{H}$ NMR spectrum of 25^+ in CDCl_3 at room temperature.

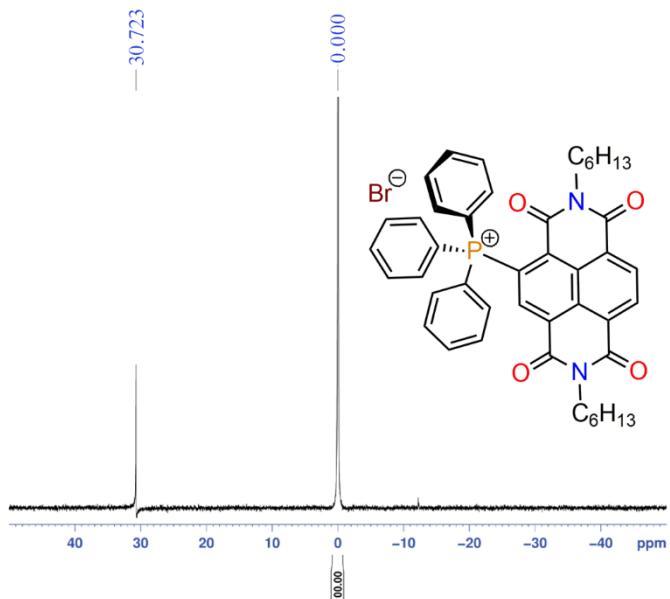


Figure S34: 202 MHz ^{31}P NMR spectrum of $\mathbf{25}^+$ in CDCl_3 at room temperature.