Materials.

The synthesis of 1,2,3,4,7,8,9,10-octahydro-1,1,4,4,7,7,10,10-octamethylnaphthacene (**OMN**) has been described previously.[11] Dichloromethane was repeatedly stirred with fresh aliquots of conc. sulfuric acid (~20 % by volume) until the acid layer remained colorless. After separation, it was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride and dried over anhydrous calcium chloride. Dichloromethane was then distilled twice from P_2O_5 under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The toluene were distilled from P_2O_5 under an argon atmosphere and then refluxed over calcium hydride (~12 h). After distillation from CaH_2, the solvents were stored in the Schlenk flasks under an argon atmosphere.

Preparation of the Monomeric Cation-Radical Salt $OMN^{+\bullet}SbF_6^-$. A 50 mL flask fitted with a Schlenk adapter was charged with nitrosonium hexafluoroantimonate (133 mg, 0.5 mmol), and a solution of **OMN** (174 mg, 0.5 mmol) in anhydrous dichloromethane (20 mL) was added under an argon atmosphere and ~0 °C. The nitric oxide produced (UV-vis spectral analysis of the gas revealed the characteristic absorbances of NO at λ_{max} = 204, 214, and 226 nm)[15] was entrained by a stream of argon. The dark-blue solution was stirred (while slowly bubbling argon through the solution) for 25 min to yield a deep-blue solution which upon spectrophotometric analysis indicated the quantitative formation of **OMN**$^{+\bullet}SbF_6^-$. The blue solution was carefully layered with dry hexane (30 mL) and placed in a refrigerator (-23 °C). During the course of 2 days, dark-blue crystals of the cation radical salt were deposited (302 mg, 0.45 mmol).

Preparation of the Heterogeneous π-Complex Cation-Radical Salt $(\mathrm{OMN}^{+\bullet})_2(\mathrm{NAP})$, $2\mathrm{SbCl}_6^-$. To a 20-mL dichloromethane solution of recrystallized **$\mathrm{OMN}^{+\bullet}$**SbCl_6^- (5×10^{-3} M) was added at –30 °C 2.5 g of solid parent naphthalene (ratio ~ 1:200). The solution, which turned from dark blue to dark green upon addition of naphthalene, was carefully layered with toluene and set up for crystallization at –23 °C. After 2 days, dark green crystals suitable for x-ray crystallography analysis were collected.

Preparation of the Solvated Cation-Radical Salt $(\mathrm{OMN}^{+\bullet})(\mathrm{toluene})_2$, SbCl_6^-. The solvated salt was obtained under conditions identical to those previously used for the isolation of the monomeric salt **$\mathrm{OMN}^{+\bullet}$**SbCl_6^-,[7f] except toluene replaced hexane as the diffusing solvent. After 3-4 days at –23 °C, dark-blue crystalline blocks of the solvated salt deposited.

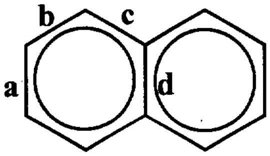
Electrocrystallization of the Parent Naphthalene Dimeric Cation-Radical salt $(\mathrm{NAP})_2^{+\bullet}\mathrm{PF}_6^-$. The experimental conditions previously described by Fritz et al.[7b] were slightly modified. In an H-shaped electrocrystallization cell placed under argon, crystals of the dimeric cation-radical salt were grown on a platinum wire electrode by anodic oxidation of a dichloromethane solution of parent naphthalene (8 mg, 5×10^{-3} M) under low constant current ($I = 1$ μA) at –45 °C in presence of $(\mathrm{NBu}_4)^+\mathrm{PF}_6^-$ (80 mg, 10^{-2} M) as supporting electrolyte.

Formation of $(\mathrm{OMN}^{+\bullet})_2(\mathrm{NAP})$, $2\mathrm{SbCl}_6^-$ in solution. A 1.8×10^{-4} M dichloromethane solution of the monomeric cation-radical salt $\mathrm{OMN}^{+\bullet}\mathrm{SbCl}_6^-$ was placed in a 1-cm quartz cuvette (UV-cell) at –78 °C. A known amount of solid parent naphthalene was incrementally added (large excess) and the UV-vis absorption spectrum was recorded after each addition. Any naphthalene addition beyond a ratio of ~1:500 resulted in a progressive decay of the UV-vis. spectrum and the experiment was stopped.

X-ray Crystallography: The intensity data for all the compounds were collected with the aid of a Siemens SMART diffractometer equipped with a CCD detector using MoK_α radiation (λ = 0.71073 Å), at -150 °C unless otherwise specified. The structures were solved by direct methods[20] and refined by full matrix least-squares procedure with IBM Pentium and SGI O_2 computers. [Note that the X-ray structure details of the various compounds mentioned here are on deposit and can be obtained from Cambridge Crystallographic Data Center, U.K.] *OMN Monomeric Cation Radical Salt* ***$OMN^{+\cdot}SbF_6^- \cdot CH_2Cl_2$***. A dark-blue crystal (0.35 x 0.20 x 0.20 mm) was selected for data collection. MW = 669.22, monoclinic $P2_1/n$, a = 8.1857(2), b = 16.8051(3), and c = 21.8905(2) Å, β = 100.423(1)°, D_c = 1.501 g cm^{-3}, V = 2961.6(1) Å^3, Z = 4. The total number of reflections measured were 35550, of which 12827 reflections were symmetrically non-equivalent. Final residuals were $R1$ = 0.0744 and w$R2$ = 0.1319 for 7124 reflections with $I > 2\sigma(I)$. *Toluene Solvate of **OMN** Monomeric Cation Radical Salt* ***$OMN^{+\cdot}SbCl_6^- \cdot 2C_7H_8$***. A dark-blue crystal (0.30 x 0.20 x 0.15 mm) was selected for data collection. MW = 867.27, monoclinic C2/c, a = 20.1705(2), b = 10.6828(1), c = 20.7359(1) Å, β = 115.205(1)°, D_c = 1.425 g cm^{-3}, V = 4042.7(1) Å^3, Z = 4. The total number of reflections measured were 24596, of which 8807 reflections were symmetrically non-equivalent. Final residuals were $R1$ = 0.0363 and w$R2$ = 0.0743 for 7493 reflections with $I > 2\sigma(I)$. *Heterogeneous π-Complex Cation Radical Salt* ***$[(OMN^{+\cdot})_2NAP(SbCl_6^-)_2$***. A dark-green crystal (0.32 x 0.20 x 0.08 mm) was selected for data collection. MW = 1664.01, orthorhombic F222 (racemic twin), a = 13.4669(2), b =

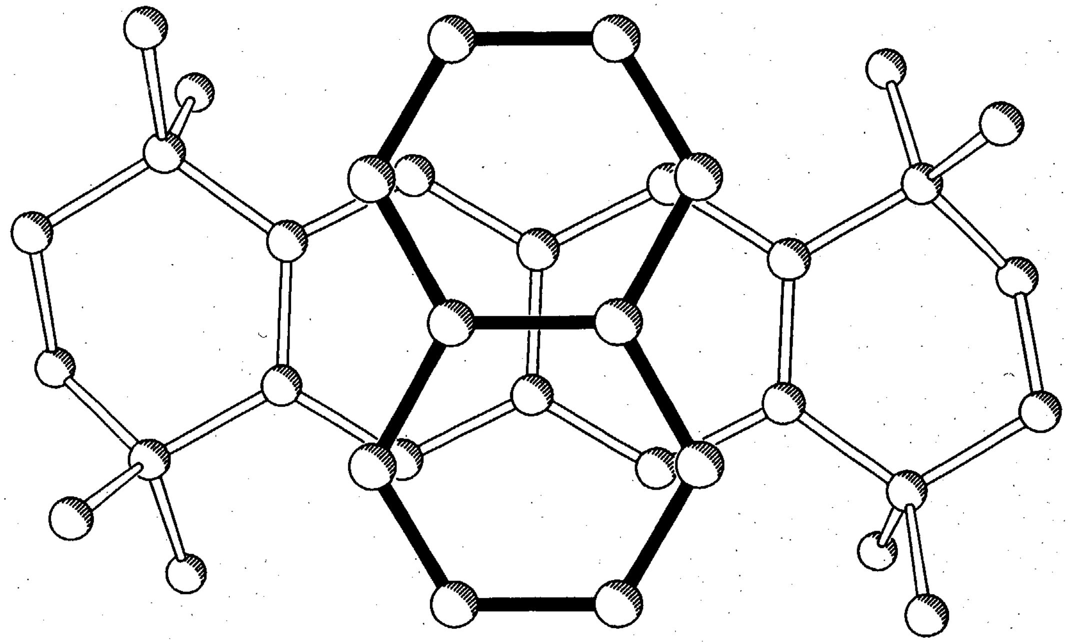
22.2481(2), c = 23.9626(2) Å, D_c = 1.534 g cm^{-3}, *V* = 7179.5(1) $Å^3$, Z = 4. The total number of reflections measured were 22975, of which 8279 reflections were symmetrically non-equivalent. Final residuals were *R*1 = 0.0686 and w*R*2 = 0.1443 for 6628 reflections with $I > 2\sigma(I)$. *Naphthalene Dimeric Cation Radical* $(NAP_2)^{+\bullet}PF_6^-$. A dark-purple crystal (0.20 x 0.20 x 0.15 mm) was selected for data collection. MW = 401.30, tetragonal $P4_2/n$, a = 11.4634(5), c = 6.3266(3) Å, D_c = 1.603 g cm^{-3}, *V* = 831.4(1) $Å^3$, Z = 2. The total number of reflections measured were 11655, of which 1852 reflections were symmetrically non-equivalent. Final residuals were *R*1 = 0.0281 and w*R*2 = 0.0778 for 1409 reflections with $I > 2\sigma(I)$.

Table S1 Interatomic bond lengths (Å) in parent **NAP** as the neutral donor, in the heteromolecular cation-radical salt [(**OMN**$^{+\bullet}$)$_2$**NAP,** 2SbCl$_6^-$) and in the dimeric cation-radical species (**NAP**)$_2^{+\bullet}$PF$_6^-$.



bond	neutral[21]	(**OMN**$^{+\bullet}$)$_2$**NAP**	(**NAP**)$_2^{+\bullet}$
a	1.413(2)	1.394(8) -1.9 pm	1.396(1) -1.7 pm
b	1.376(2)	1.382(5) +0.6 pm	1.387(1) +1.1 pm
c	1.423(2)	1.411(4) -1.2 pm	1.413(1) -1.0 pm
d	1.422(2)	1.420(9) +0.2 pm	1.422(1) +0.0 pm

Figure S1



Top perspective of the heteromolecular cation-radical complex showing the degree of π, π-overlap between **NAP** and **OMN**$^{+\bullet}$ moieties.. Hydrogens omitted for clarity