ESI contains:

1/ Figures S1, S2 and S3
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3/ Pulsed EPR nutation measurements by PEANUT experiment
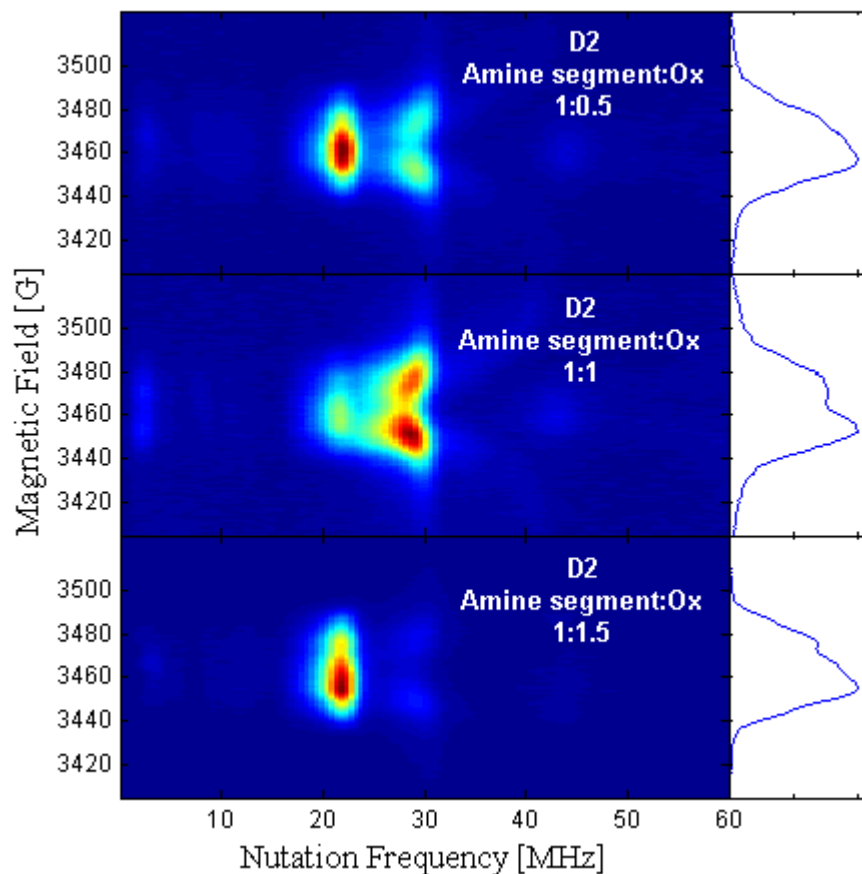4/ SQUID magnetometry.
5/ DFT methodology

1/ Figures S1 and S2

Figure S1. **Pulsed-EPR nutation spectra** of D2 samples (concentration: $5 \cdot 10^{-3}$ mol.L^{-1}) in acetonitrile:chloroform 1:1 solutions, doped with 0.5 equivalent (upper), 1.0 equivalent (middle) and 1.5 equivalent (lower) of oxidant per amine segment unit. Spectra are recorded at T=7K. The frame on the right of each 2D spectrum is the projection spectrum: sum of nutation signals recorded vs. magnetic field.
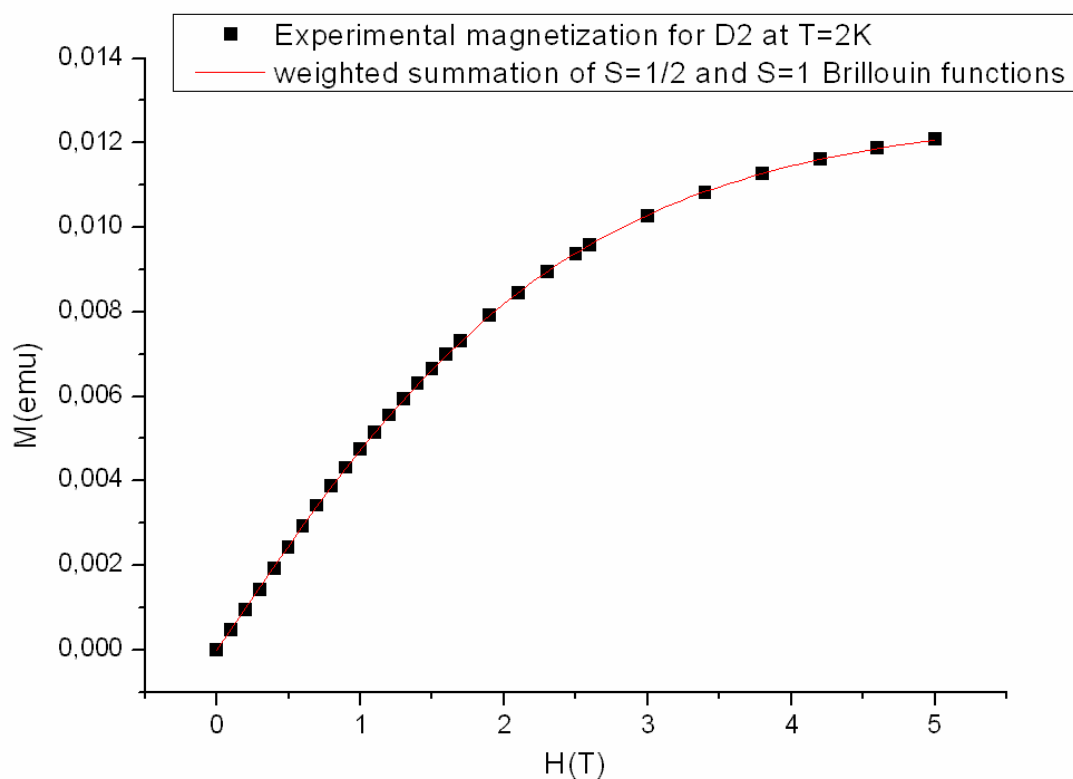
Figure S2. **Numerical fitting of M=f(H) experiments for a stoechiometrically doped D2 sample.** The M=f(H) curve is the same as this reported in Figure 3B and corresponds to a D2 sample at T=2K with D2 concentration $3 \cdot 10^{-2}$ mol.L^{-1} in acetonitrile:chloroform 1:1 solution and doped with 1.0 equivalent of oxidant per amine segment unit. The numerical fitting shown in this figure was performed with the weighted summation of Brillouin Functions for S=1 and S=1/2 spin systems. This numerical fitting provides the following results: $1.1.10^{-6}$ mol of S=1/2 spins and $5.7 \ 10^{-7}$ mol of S=1 for a sample containing $1.7 \ 10^{-6}$ mol of D2. These results correspond to 66% of D2 dimers in S=1/2 state and 34% of D2 dimers in S=1 state.
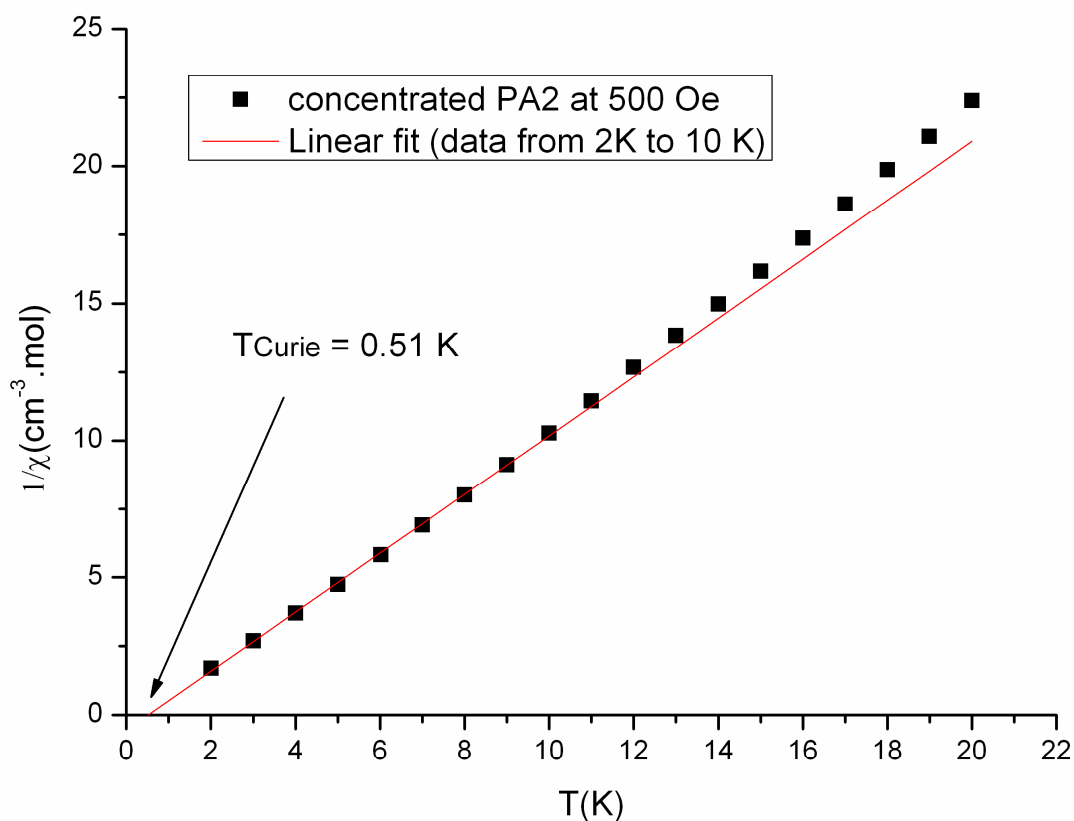
Figure S3. **$1/\chi$ versus temperature at 500 Oe of PA2 sample doped with one equivalent of oxidant per conjugated amine segment**. The SQUID measurements of the same PA2 sample ($3 \cdot 10^{-2}$ mol.L^{-1}) is described in Figure 3 and 4 and this sample is referred in the main text as "concentrated PA2". In red, linear fit corresponding to the equation $1/\chi = \text{constant}.(T - T_{Curie})$ performed for experimental points between 2K and 10K.

This plot is drawn to check that the weak intermolecular ferromagnetic interactions observed in $\chi T = f(T)$ plots of concentrated PA2 samples (see Fig . 4 C) and modelled by $zJ'=0.44K$ in equation (1) can also be modelled consistently by a mean-field theory and the Curie-Weiss law:

$$1/\chi = \text{constant}.(T - T_{Curie}).$$

In order to find the T_{Curie} corresponding to weak interactions between S=1 spins, only data recorded for low enough temperature (T<<J) should be considered (J=18 K in the case of PA2). Moreover only data recorded for high enough temperature (T>>T_{Curie}) should be considered, so we considered data in the range 2K $\leq$ T $\leq$10 K.

From the linear fitting of experimental data with the Curie-Weiss law, we find $T_{Curie} = 0.51$ K, which is in good agreement with $zJ'=0.44K$ obtained from the analysis of the $\chi T=f(T)$ plot**.**

2/ Procedures of chemical synthesis and chemical doping

Characterization techniques.

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury (400 and 100 MHz) spectrometer and referenced with respect to TMS and solvents. IR spectra were monitored on Bio-RAD FTS-165 spectrometer using KBr pellets. UV-Vis-NIR spectra were registered using a Cary 5000 (Varian) spectrometer. Mass spectra were measured by EI method on an AMD 604 mass spectrometer. All synthesized compounds studied were subject to C, H, N and Br elemental combustion analysis.

Reagents

4-butylaniline, 4-*tert*-butylaniline, bromobenzene, 1,4-dibromobenzene, 1-bromo-4-butylbenzene, 1,3-dibromobenzene, palladium acetate, (Pd(OAc)$_2$), tris-*tert*-butylphosphine, (*t*-Bu$_3$P), 2,2'—bis(diphenylphosphino)-1,1'-binaphtyl, (BINAP), sodium *tert*-butoxide, (*t*-BuONa), di-*tert*-butyl dicarbonate, (BOC), N-bromosuccinimide, (NBS), trifluoroacetic acid, (TFA), N,N-dimethylformamide, (DMF), anhydrous toluene, anhydrous acetonitrile were purchased from Aldrich. 4-Butylaniline and 4-*tert*-butylaniline were distilled under reduced pressure. N-bromosuccinimide (NBS) was crystallized from water.

All glassware was oven dried, assembled hot, and cooled under a dry argon stream before use. All reactions were performed under dry argon.

General procedure for C-N bonding formation

Palladium acetate (3%$_{mol}$) and phosphine (9%$_{mol}$) were mixed in 5 mL of dry toluene and stirred under an argon atmosphere for 0.5 h. Then aryl bromide (1 mmol), amine (1 mmol), sodium *tert*-butoxide (1.5 mmol) and *ca.* 10 mL of dry toluene were added to the reaction flask. The mixture was stirred and heated at 110 °C for 20 h. After the mixture was cooled to room temperature, 50 mL of distilled water was added and the organic layer separated. The aqueous phase was extracted with three 10 mL portions of diethyl ether. The combined organic phases were dried over MgSO$_4$.

Dimer, D2

The titled compound was prepared according to the procedure presented in Scheme 1.
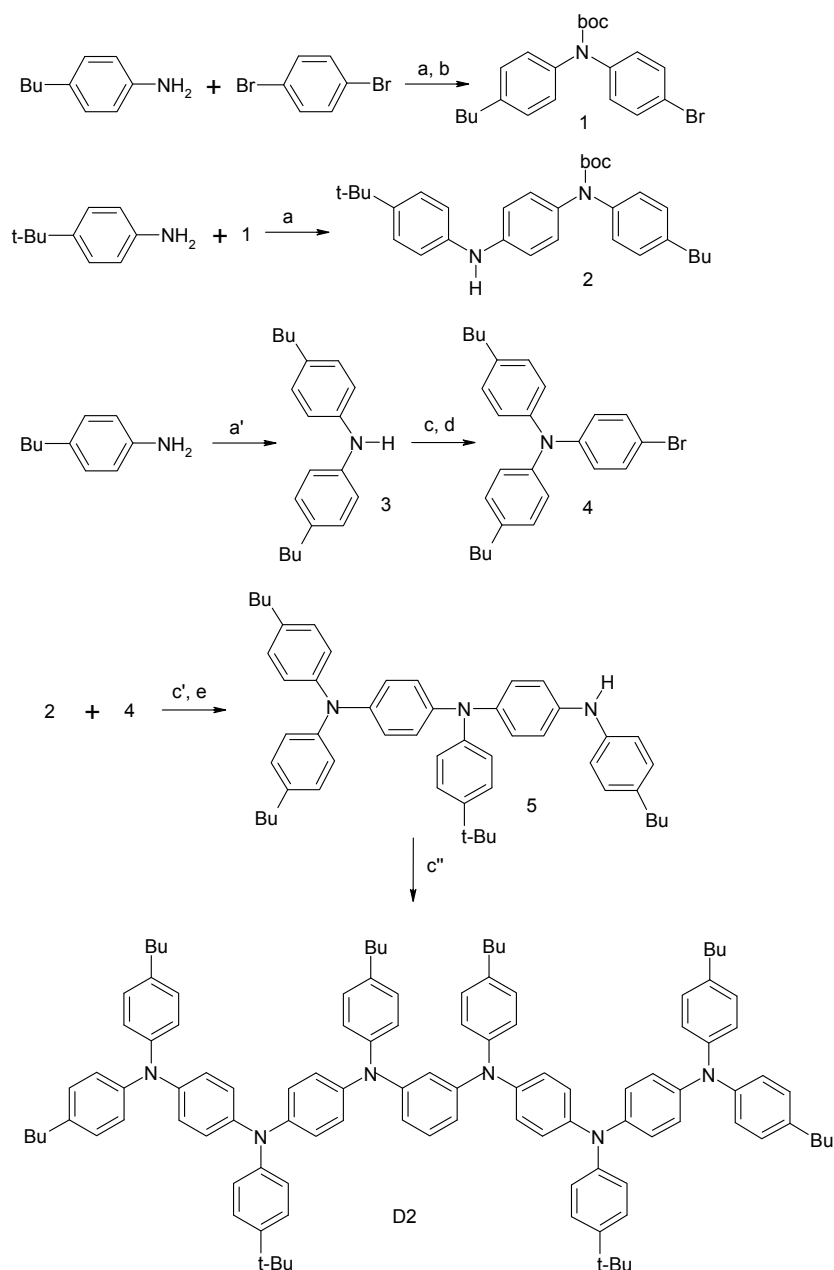
Scheme 1. The synthesis of dimer 2: a) Pd(OAc)$_2$, BINAP, NaOt-Bu, toluene, 110 ºC, a') 1-bromo-4-butylbenzene, Pd(OAc)$_2$, BINAP, NaOt-Bu, toluene, 110 ºC, b) BOC, DAMP, THF, reflux, c) bromobenzene, Pd(OAc)$_2$, t-Bu$_3$P, NaOt-Bu, toluene, 110 ºC, c') Pd(OAc)$_2$, t-Bu$_3$P, NaOt-Bu, toluene, 110 ºC, c'') 1,3-dibromobenzene, Pd(OAc)$_2$, t-Bu$_3$P, NaOt-Bu, toluene, 110 ºC, d) NBS, DMF, RT, e) TFA.

(4-Butylphenyl)-(4'-bromophenyl)-N-(*tert*-butoxycarbonyl)amine 1

Palladium acetate, 202 mg (0.9 mmol) and BINAP, 1.68 g (2.7 mmol) were mixed in 5 mL of dry toluene and stirred under an argon atmosphere for 0.5 h. Then 1,4-dibromobenzene, 7.08 g (30 mmol), 4-butylaniline, 4.47 g (30 mmol), sodium *tert*-butoxide, 4.05 g (42 mmol) and *ca.* 55 mL of dry toluene were added to the reaction flask. The mixture was stirred and heated at 110 °C for 20 h. After the evaporation of solvents the crude product was purified by chromatography on silica gel eluting with CH$_2$Cl$_2$/hexanes (1:1) and then recrystallized in

ethyl acetate/methanol to give 8.87 g (29.2 mmol, 97.3% yield) of (4-butylphenyl)-(4'-bromophenyl)amine. The resulting product was mixed with 4-(dimethylamino)pyridine, 0.73 g (5.8 mmol, 20%$_{mol.}$), di-*tert*-butyl dicarbonate, 9.52 g (43.68 mmol) in 45 mL of dry THF. The mixture was heated to reflux for 3 h. After evaporation of the solvents the product was purified by chromatography eluting with CH_2Cl_2/hexanes (1:1) to give a slightly yellow oil, 10.02 g (24.8 mmol, 85% yield). Mp. 38.3-40.5 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ, 7.41-7.38 (m, 2H), 7.13-7.06 (m, 6H), 2.58 (t, J=7.6 Hz, 2H), 1.58-1.54 (m, 2H), 1.44 (s, 9H), 1.38-1.31 (m, 2H), 0.92 (t, J=7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ, 142.3, 140.8, 140.1, 131.6, 128.8, 128.2, 126.9, 118.6, 81.4, 35.1, 33.5, 28.2, 27.9, 22.3, 13.9. IR (cm^{-1}): 3005, 2982, 2931, 2868, 1706, 1513, 1490, 1336, 1164, 1055, 830. Anal. Calcd for $C_{21}H_{26}BrNO$: C, 62.39; H, 6.44; N, 3.47; Br, 19.78. Found: C, 62.88; H, 6.68; N, 3.56; Br, 19.84.

N-(4-*tert*-butylphenyl)-N'-(4'-butylphenyl)-N'-(*tert*-butoxycarbonyl)-1,4-phenylenediamine, 2

Pd(OAc)$_2$ 2, 13.5 mg (0.006 mmol) and BINAP, 112 mg (0.18 mmol) were mixed in 5 mL of dry toluene under an argon atmosphere for 0.5 h at room temperature. Compound **1**, 0.805 g (2 mmol), 4-*tert*-butylaniline, 0.3 g (2 mmol), sodium *tert*-butoxide, 0.29 g (3 mmol) and 10 mL of dry toluene were added to the reaction flask. The mixture was stirred and heated at 110 °C for 20 h. Then the mixture was cooled to room temperature, washed with brine and extracted with three 10 mL portions of diethyl ether. The combined organic layers were dried over MgSO$_4$. After evaporation of the solvents the crude product was purified by chromatography on silica gel eluting with CH_2Cl_2/hexanes (1:1) and then recrystallized in ethyl acetate/methanol to give 0.89 g (1.88 mmol, 94% yield) of white powder. Mp. 108.5-109.5 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$) δ, 7.34 (d, J=8.4 Hz, 2H), 7.19-7.16 (m, 4H), 6.99 (d, J=8 Hz, 2H), 6.84 (d, J=8.8 Hz, 2H), 6.74 (d, J=9.2 Hz, 2H), 4.95 (s, 1H), 2.39 (t, J=7.8 Hz, 2H), 1.43 (s, 9H), 1.40-1.38 (m, 2H), 1.25 (s, 9H), 1.23-1.17 (m, 2H), 0.81 (t, J=7.4 Hz, 3H). ^{13}C NMR (100 MHz, C$_6$D$_6$) δ, 154.0, 144.1, 142.0, 140.6, 139.8, 136.5, 128.8, 128.5, 126.9, 126.3, 118.8, 117.1, 81.1, 35.4, 33.8, 31.6, 28.3, 22.6, 14.1. IR (cm^{-1}): 3352, 3028, 2956, 2872, 1685, 1606, 1513, 1315, 1160, 1056, 825. Anal Calcd for $C_{31}H_{39}N_2O_2$; C, 78.94; H, 8.33; N, 5.95; O, 6.78. Found: C, 78.68; H, 8.23; N, 5.93.

Di(4-butylphenyl)amine, 3

4-Butylaniline, 2.98 g (20 mmol), 1-bromo-4-butylbenzene, 4.69 g (22 mmol), sodium *tert*-butoxide, 2.88 g (30 mmol), palladium acetate, 134.7 mg (0.6 mmol) and BINAP, 1.12 g (1.8 mmol) were dissolved in 40 mL of dry toluene under an argon atmosphere. The reaction mixture was stirred and heated at 110 °C for 20 h. Removal of the solvents followed by chromatography on silica gel (CH_2Cl_2/hexanes, 1:2, containing 1%$_v$ of Et$_3$N) resulted in pale yellow oil, 5.15 g (18.3 mmol, 91.6% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$) δ,7.01-7.00 (m, 4H), 6.91-6.88 (m, 4H), 4.98 (s, 1H), 2.48 (t, J=7.6 Hz, 4H), 1.56-1.48 (m, 4H), 1.33-1.23 (m, 4H), 0.87 (t, J=7.4 Hz, 6H). ^{13}C NMR (100 MHz, C$_6$D$_6$) δ, 141.9, 135.2, 129.5, 118.2, 35.3, 34.2, 22.6, 14.1. IR (cm^{-1}): 3397, 3025, 2957, 2928, 2856, 1610, 1516, 1458, 1310, 823. Anal Calcd for $C_{20}H_{27}N$; C, 85.41; H, 9.61; N, 4.98. Found: C, 85.01; H, 9.37; N, 5.60.

Di(4-butylphenyl)-4'-bromophenylamine, 4

Pd(OAc)$_2$, 40.4 mg (0.18 mmol) and tri-*tert*-butylphosphine, 109.2 mg (0.54 mmol) were dissolved in 5 mL of dry toluene under an argon atmosphere and stirred at room temperature for 15 min. Bromobenzene, 0.97 g (6.2 mmol), amine **3**, 1.645 g (5.85 mmol), sodium *tert*-

butoxide, 0.69 g (7.2 mmol) and 15 mL of dry toluene were added to the reaction flask. The mixture was stirred and heated at 110 °C for 20 h. The crude product was chromatographed eluting with CH_2Cl_2/hexanes, (1:2) to give 1.99 g (5.57 mmol, 95.3% yield) of colorless oil. The oil was dissolved in 10 mL of dry DMF under an argon atmosphere. NBS, 0.99 g (5.57 mmol) was dissolved in 10 mL of dry DMF and placed in a funnel. NBS solution was added dropwise from a funnel to the solution of amine, stirred at room temperature. After 1.5 h of stirring, 50 mL of distilled water was added to form an emulsion which was extracted with three 10 mL portions of diethyl ether. The combined organic layers were washed with brine, then with water and dried over $MgSO_4$. After evaporation of the solvent the titled compound **4** was obtained as a colorless oil, 2.3 g (5.29 mmol, 95% yield). ^{1}H NMR (400 MHz, C_6D_6) δ, 7.12 (d, J=8.8 Hz, 2H), 7.04-7.01 (m, 4H), 6.94-6.92 (m, 4H), 6.79 (d, J=9.2 Hz, 2H), 2.42 (t, J=7.8 Hz, 4H), 1.50-1.43 (m, 4H), 1.29-1.20 (m, 4H), 0.83 (t, J=7.2 Hz, 6H). ^{13}C NMR (100 MHz, C_6D_6) δ, 147.8, 145.7, 138.1, 132.3, 129.5, 125.0, 124.7, 114.3, 35.4, 34.1, 22.7, 14.1. IR (cm^{-1}): 3028, 2957, 2928, 2871, 1606, 1584, 1508, 1486, 1312, 1281, 821. Anal Calcd for $C_{26}H_{30}NBr$: C, 71.55; H, 6.93; N, 3.21; Br, 18.31. Found: C, 71.12; H, 6.83; N, 3.10; Br, 18.93.

Compound, 5

$Pd(OAc)_2$, 11.4 mg (0.051 mmol) and *tert*-Bu_3P, 31 mg (0.153 mmol) were dissolved in 5 mL of dry toluene under an argon atmospher for 15 min. Compound **4**, 0.685 g (1.57 mmol), compound **2**, 0.74 g (1.57 mmol), sodium *tert*-butoxide, 0.245 g (2.55 mmol) and 10 mL of dry toluene were added to the reaction flask. The mixture was stirred and heated at 110 °C for 20 h. The crude product was purified by chromatography eluting with CH_2Cl_2/hexanes (3:1, with 1%$_v$ of Et_3N). The product was dissolved in 15 mL of trifluoroacetic acid and stirred for 0.5 h at room temperature. TFA was evaporated and the residue was dissolved in 5 mL of toluene. 20 mL of 1 M NaOH aqueous solution was added to the toluene solution and vigorously stirred for 20 min. The organic phase was extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$. The evaporation of the solvents resulted in 1.13 g (1.55 mmol, 98.7% yield) of pale yellow solid. ^{1}H NMR (400 MHz, C_6D_6) δ, 7.22-7.19 (m, 8H), 7.13-7.09 (m, 6H), 7.00-6.94 (m, 6H), 6.85 (d, J=8.4 Hz, 2H), 6.76 (d, J=8.8 Hz, 2H), 4.92 (s, 1H), 2.48-2.36 (m, 6H), 1.58-1.43 (m, 6H), 1.29-1.25 (m, 6H), 1.23 (s, 9H), 0.89-0.82 (m, 9H). ^{13}C NMR (100 MHz, C_6D_6) δ, 146.6, 146.5, 143.8, 143.0, 141.6, 139.7, 137.0, 136.6, 135.3, 129.5, 126.5, 125.4, 124.2, 123.7, 118.9, 118.3, 35.3, 34.2, 22.6, 14.1. IR (cm^{-1}): 3389, 3032, 2958, 2927, 2856, 1613, 1506, 1465, 1313, 1271, 823. Anal Calcd for $C_{52}H_{61}N_3$: C, 85.78; H, 8.44; N, 5.78. Found: C, 85.88; H, 8.76; N, 6.02.

Dimer, D2

The same procedure as previously was followed using 0.925 g (1.27 mmol) of amine **5**, 0.15 g (0.636 mmol) of 1,3-dibromobenzene, 0.225 g (2.34 mmol) of sodium *tert*-butoxide, 10.5 mg (0.047 mmol) of $Pd(OAc)_2$, 28.5 mg (0.141 mmol) of *tert*-Bu_3P and 15 mL of dry toluene. The crude product was purified by chromatography eluting with CH_2Cl_2/hexanes (1:2, with 1%$_v$ of Et_3N) to give 1.37 g (0.9 mmol, 70.9% yield) of white solid. The product was additionally purified by chromatography eluting with CH_2Cl_2/hexanes (1:9 with 0.5%$_v$ of diethyl ether and 1%$_v$ of Et_3N). Mp 95.2-96.2 °C. ^{1}H NMR (400 MHz, C_6D_6) δ, 7.20-7.17 (m, 18H), 7.08-7.03 (m, 17H), 6.97-6.91 (m, 15H), 6.80 (dd, J=8.0, 2.0 Hz, 2H), 2.45-2.40 (m, 12H), 1.52-1.43 (m, 12H), 1.29-1.18 (m, 30H), 0.87-0.82 (m, 18H). ^{13}C NMR (100 MHz, C_6D_6) δ, 149.5, 146.4, 146.0, 145.8, 145.2, 143.6, 143.5, 143.1, 142.8, 137.5, 137.1, 129.6, 126.4, 125.3, 125.2, 125.1, 124.4, 123.9, 35.4, 34.1, 31.5, 22.7, 14.1. IR (cm^{-1}): 3032, 2957,

2928, 2856, 1607, 1591, 1501, 1465, 1314, 1267, 828. Anal Calcd for $C_{110}H_{124}N_6$: C, 86.34; H, 8.17; N, 5.49. Found: C, 86.51; H, 8.02; N, 5.42. M/z=1530.1.

Hexaazacyclophane, C2

The titled compound was prepared according to the procedure described in[1].

Polymer, PA2

The polymer was prepared following the reaction presented in[2].

Oxidation procedure for pulsed EPR and SQUID experiments

The chemical oxidation of PA2 was carried out in an argon atmosphere. In a typical procedure 1 mL of 0.01 M (molar concentration of the mer) solution of PA2 in chloroform was oxidized with the appropriate amount of 0.01 M oxidant solution in acetonitrile. Then 100 μL of the oxidized solution were used for pulsed EPR spectroscopy and 60 μL were used for SQUID magnetometry experiments reported as "diluted samples". For all other SQUID magnetometry (reported as "concentrated samples") the oxidized solution was dried under vacuum, re-dissolved in 350 μL of chloroform:acetonitrile (1:1), then 60 μL were collected for SQUID experiments. Similar procedures were used for experiments with D2 and C2.

3/ Pulsed EPR nutation measurements by PEANUT experiment

Nutation pulsed EPR experiments were performed using a Bruker Elexsys 580 EPR spectrometer in pulsed mode at 7 K. The PEANUT experiment (phase-inverted echo amplitude detected nutation) introduced by Stoll et al.[3] was used in order to achieve an optimal resolution of nutation frequencies in the recorded spectra.

The PEANUT experiment is described in Scheme 2. In a typical experiment the first pulse used was a selective low power pulse ($B_1 \sim 0.7$ G). This pulse was set up to be a true $\pi/2$ pulse for species having nutation frequencies twice higher than S=1/2 species in order to better detect signals of S=3/2 and S=2 species. Two steps phase cycling (+x, –x) was performed on this first pulse. The high turning angle pulses ($B_1 \sim 7$ G) had a constant length of 1536 ns and the x pulse (–x pulse) was incremented (decremented) by 256 steps of 2 ns, respectively. At every step, the spin rotary echo was integrated using a 76 ns gate centred at its maximum.
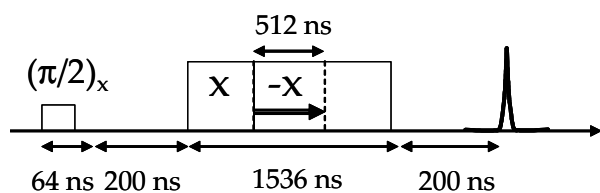
Scheme 4. Pulses sequence used for the PEANUT experiments.

The obtained time-domain oscillating signal was treated with second order polynomial baseline correction, sinebell transformation and symmetrical zero-filling (256 zeroes added). Then it was Fourier transformed using a numerical FFT software to yield the corresponding nutation spectrum. Two dimensions maps (Magnetic Field vs. Nutation spectrum) were obtained by successively performing PEANUT experiments at 200 magnetic field values spaced by steps of one Gauss.

The spin multiplicities of detected species were obtained by comparing the measured nutation frequency (ν_{nut}) to the nutation frequency previously measured for a known S=1/2 systems ($\nu_{S=1/2}$) and using the following relationship:

$$\nu_{nut} = \sqrt{S(S+1) - m_S(m_S+1)} \cdot \nu_{S=1/2} \qquad (1)$$

This relationship is given for an EPR $\left| S, m_s \right\rangle \longleftrightarrow \left| S, m_s + 1 \right\rangle$ transition and is valid for low magnetic field excitation ($B_1 \ll D$, D the axial zero field splitting parameter of the considered species)[4].

4/ SQUID magnetometry.

The SQUID magnetometry experiments were performed with a Quantum Design MPMS XL 5.0 SQUID magnetometer. The frozen solution samples were contained in a quartz tube (4 mm diameter with flat extremity) sealed under vacuum and maintained by a sample quartz sample holder designed to minimize the diamagnetic contribution to magnetization measurements. The residual diamagnetic contributions due to the quartz tube and the sample holder and the diamagnetic magnetization of the solvent (60µL of chloroform:acetonitrile 1:1) were measured in blank experiments and were used to subtract the diamagnetic contribution from the magnetizations measured with solutions of doped polymer and dimers .

5/ DFT methodology

For the two systems C2 and D2 we carried out molecular dynamic (MD) simulations to find the structures of lowest energies. The dynamics has been performed with the TINKER MD software using the oplsaa force field designed for proteins and many general classes of organic molecules. NPT-simulations (constant number of moles, pressure and temperature) in vacuum have been performed at 298 K during 1 ns for the neutral forms of C2 and D2.

From the MD trajectories we selected the lower geometries for C2 and D2 which differ by less than 5 kcal/mol from the lowest energy conformation in each case. The superposition of these geometries showed one unique conformation for each compound.

Quantum mechanics (QM) density functional theory (DFT) geometry optimizations have been further performed using the ADF package[5] (2009) with the VBP functional[6] (Vosko, Wilk and Nusair's exchange and correlation energy completed by non local gradient corrections to the exchange by Becke as well as to the correlation by Perdew). We used a triplet-ζ basis set for all atoms and the QM geometries optimisations have been done for the di-cation forms of $C2^{2+}$ and $D2^{2+}$ in their triplet states. Finally we use the standard B3LYP exchange correlation potential[7, 8] to compute triplet and broken symmetry states from which we extract exchange coupling constants $J_{BS}=2(E_{BS}-E_T)$ as prescribed by Noodleman[9].

From the ADF TAPE21 output file and a homemade Python code, the magnetic orbitals, i.e. the spin density distributions of the unpaired electron in the broken symmetry state has been represented.

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