## Supporting Information

A Simple Route to the Doubly ortho-Palladated Azobenzenes: Building Blocks for Organometallic Polymers and Metallomesogens

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## Experimental procedures

All chemicals and solvents used for the syntheses were commercially available. The yields of prepared complexes are based on azobenzenes since Pd is used in excess.

Preparation of $\{\mathbf{P d C l}(\mathbf{d m f})\}_{\mathbf{2}}\left(\mu-\mathbf{C}_{\mathbf{6}} \mathbf{H}_{\mathbf{4}} \mathbf{N}=\mathbf{N C}_{\mathbf{6}} \mathbf{H}_{\mathbf{4}}\right)(\mathbf{1}) . \mathrm{PdCl}_{2}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{2}(213 \mathrm{mg}, 0.82 \mathrm{mmol})$ was dissolved in ( 3 mL ) dimethylformamide (dmf) and added to a solution ( 2 mL ) of azobenzene in dmf ( 50 $\mathrm{mg}, 0.27 \mathrm{mmol}$ ). The mixture was stirred at room temperature for three days and then a new dmf solution ( 2 mL ) of $\mathrm{PdCl}_{2}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{2}(142 \mathrm{mg}, 0.55 \mathrm{mmol})$ was added. The stirring of the resulting mixture continued for three more days. The dark red precipitate was filtered off and dried under vacuum. Yield 70\%. Anal. Calcd. (found) for $\mathrm{C}_{18} \mathrm{H}_{22} \mathrm{~N}_{4} \mathrm{O}_{2} \mathrm{Pd}_{2} \mathrm{Cl}_{2}$ : C, 35.43 (34.90); H, 3.61 (3.50); N, 9.18 (8.98).

Preparation of $\{\mathbf{P d C l}(\mathbf{d m f})\}_{\mathbf{2}}\left(\mu-\mathbf{C}_{\mathbf{6}} \mathbf{H}_{\mathbf{4}} \mathbf{N}=\mathbf{N C}_{\mathbf{6}} \mathbf{H}_{\mathbf{3}} \mathbf{N H}_{\mathbf{2}}\right) \mathbf{( 2 )} . \mathrm{PdCl}_{2}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{2}(197 \mathrm{mg}, 0.76 \mathrm{mmol})$ was dissolved in ( 3 mL ) dmf and added to a solution ( 2 mL ) of azobenzene in $\mathrm{dmf}(50 \mathrm{mg}, 0.25 \mathrm{mmol})$. The mixture was stirred at room temperature for three days and then a new dmf solution ( 2 mL ) of $\mathrm{PdCl}_{2}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{2}(131 \mathrm{mg}, 0.51 \mathrm{mmol})$ was added. The stirring of the resulting mixture continued for three more days. The brown red precipitate was filtered off and dried under vacuum. Yield $90 \%$. Anal. Calcd. (found) for $\mathrm{C}_{18} \mathrm{H}_{23} \mathrm{~N}_{5} \mathrm{O}_{2} \mathrm{Pd}_{2} \mathrm{Cl}_{2}$ : C, 34.58 (34.13); $\mathrm{H}, 3.68$ (3.20); $\mathrm{N}, 11.21$ (10.88).

Preparation of $\{\mathbf{P d C l}(\mathbf{d m s o})\}_{\mathbf{2}}\left(\mu-\mathbf{C}_{\mathbf{6}} \mathbf{H}_{\mathbf{4}} \mathbf{N}=\mathbf{N C}_{\mathbf{6}} \mathbf{H}_{\mathbf{4}}\right)$ (3). The complex $\mathbf{1}(50 \mathrm{mg}, 0.08 \mathrm{mmol})$ was dissolved in ( 30 mL ) warm dimethyl sulfoxide (dmso). The solution was filtered off and allowed to stand at room temperature for one week. The red crystals were obtained in a yield $55 \%$. Anal. Calcd. (found) for $\mathrm{C}_{16} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{~S}_{2} \mathrm{O}_{2} \mathrm{Pd}_{2} \mathrm{Cl}_{2}$ : C, 30.98 (30.82); $\mathrm{H}, 3.23$ (3.50); $\mathrm{N}, 4.52$ (4.26).

Preparation of $\{\mathbf{P d C l}(\mathbf{d m s o})\}_{\mathbf{2}}\left(\mu-\mathbf{C}_{\mathbf{6}} \mathbf{H}_{\mathbf{4}} \mathbf{N}=\mathbf{N C}_{\mathbf{6}} \mathbf{H}_{\mathbf{3}} \mathbf{N H}_{\mathbf{2}}\right) \mathbf{( 4 )}$. The complex $\mathbf{2}(50 \mathrm{mg}, 0.08 \mathrm{mmol})$ was dissolved in warm dmso ( 30 mL ). The solution was filtered off and allowed to stand at room temperature for four weeks. The brown red crystals were obtained in a yield 63\%. Anal. Calcd. (found) for $\mathrm{C}_{16} \mathrm{H}_{21} \mathrm{~N}_{3} \mathrm{~S}_{2} \mathrm{O}_{2} \mathrm{Pd}_{2} \mathrm{Cl}_{2}$ : C, 30.24 (29.90); H, 3.31 (3.48); $\mathrm{N}, 6.62$ (6.98).

NMR spectra. The one- and two-dimensional ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded in dmso- $\mathrm{d}_{6}$ and/or in dmf $-\mathrm{d}_{7}$ with Brucker AV-600 spectrometer, operating at 600.13 for the ${ }^{1} \mathrm{H}$ and 150.90 MHz for the ${ }^{13} \mathrm{C}$ resonances. The ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY spectra were obtained in the magnitude mode with 2048 points in the $F 2$ dimension and 512 increments in the $F 1$ dimension. The ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ HMQC spectra were measured with one-bond C,H coupling value set to 145 Hz , using 2048 points in the $F 2$ dimension and 256 increments in the $F 1$ dimension. The ${ }^{1} \mathrm{H}^{13} \mathrm{C}$ HMBC spectra were measured with C,H coupling value set to 145 and 8 Hz using 2048 points in the $F 2$ dimension and 256 increments in the $F 1$
dimension. All two-dimensional experiments were performed by standard pulse sequences using Brucker XWIN-NMR software Version 3.5. Waltz 16 modulation was used for proton decoupling.

X-ray structure analysis: The single-crystals of complexes $\mathbf{1}$ and 4, suitable for X-ray measurement, were prepared in dmf and dmso, respectively. Attempts to prepare suitable crystals of complexes 2 and $\mathbf{3}$ were unsuccessful. Crystal data and other crystallographic experimental details are summarized in Table 3. Both data collections were performed on an Enraf Nonius CAD4 diffractometer using graphite monochromated $\mathrm{Cu} K_{\alpha}$ radiation ( $\lambda=1.54179 \AA$ ). During the data collections the control reflections measured every 120 min did not show any significant loss of intensity. The raw intensities were corrected for Lorentz, polarization and absorption effect using the WinGX data reduction routines. ${ }^{1}$ The structures were solved and refined with SHELXL-97. ${ }^{2}$ Hydrogen atoms were included in structure calculations as riding entities. For all non-hydrogen atoms anisotropic thermal factors were refined. The final Fourier maps revealed maximum residuals of 1.229 in 1 and 1.088 in 4, both close to the Pd atoms. CCDC-270786 and CCDC-270787 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Ab initio calculations. Preliminary calculations have been performed with Gaussian $03^{3}$ by combining closed shell RHF and DFT (B3LYP) methods with two basis sets of different sizes. The smaller basis consisted of $\mathrm{D}_{2} 5 \mathrm{~V}^{4}$ basis functions on $\mathrm{H}, \mathrm{C}, \mathrm{N}$ and O atoms and Los Alamos pseudopotentials (ECP) with $\mathrm{DZ}^{5}$ basis functions on $\mathrm{S}, \mathrm{Cl}$ and Pd atoms. In the larger basis set, Los Alamos ECP with DZ basis functions on only Pd atom were combined with $6-31 \mathrm{G}(\mathrm{d}, \mathrm{p})$ basis on all other atoms. The final computations were done by B3LYP method and larger basis. All geometries were fully optimized and the minima were verified by frequency calculations.

## Scheme S1




Figure S1. The atom numbering of azobenzenes used in the assignment of NMR resonances.

Table S1. ${ }^{1} \mathrm{H}$ NMR data in DMSO ( $\delta \mathrm{ppm}, J \mathrm{~Hz}$ )

| H | Compound ${ }^{\text {a }}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | $\mathbf{a z b}^{\text {b }}$ | $\mathbf{a a z b}^{\text {c }}$ | $1^{\text {d }}$ (3) ${ }^{\text {f }}$ | $2^{\text {e }}(4)^{\text {f }}$ |
| H-2 | $7.89 \mathrm{~d} \quad J(\mathrm{HH})=6.9$ | $7.68 \mathrm{~d} \quad J(\mathrm{HH})=8.4$ |  |  |
| H-3 | $7.60 \mathrm{t} \quad J(\mathrm{HH})=7.0$ | $6.70 \mathrm{~d} \quad J(\mathrm{HH})=8.5$ | $8.74 \mathrm{~d} \quad J(\mathrm{HH})=7.2$ | 7.04 s |
| H-4 | $7.58 \mathrm{t} \quad J(\mathrm{HH})=6.6$ |  | $7.24 \mathrm{t} \quad J(\mathrm{HH})=7.9$ |  |
| H-5 | $7.60 \mathrm{t} \quad J(\mathrm{HH})=7.0$ | $6.70 \mathrm{~d} \quad J(\mathrm{HH})=8.5$ | $7.21 \mathrm{t} \quad J(\mathrm{HH})=7.4$ | $6.35 \mathrm{~d} \quad J(\mathrm{HH})=8.9$ |
| H-6 | $7.89 \mathrm{~d} J(\mathrm{HH})=6.9$ | $7.68 \mathrm{~d} \quad J(\mathrm{HH})=8.4$ | $7.87 \mathrm{~d} \quad J(\mathrm{HH})=7.3$ | $8.41 \mathrm{~d} J(\mathrm{HH})=9.1$ |
| H-8 | $7.89 \mathrm{~d} J(\mathrm{HH})=6.9$ | $7.75 \mathrm{~d} \quad J(\mathrm{HH})=7.8$ |  |  |
| H-9 | $7.60 \mathrm{t} \quad J(\mathrm{HH})=7.0$ | $7.50 \mathrm{t} \quad J(\mathrm{HH})=7.6$ | $8.74 \mathrm{~d} \quad J(\mathrm{HH})=7.2$ | $8.22 \mathrm{~d} J(\mathrm{HH})=7.9$ |
| H-10 | $7.58 \mathrm{t} \quad J(\mathrm{HH})=6.6$ | $7.41 \mathrm{t} \quad J(\mathrm{HH})=7.4$ | $7.24 \mathrm{t} \quad J(\mathrm{HH})=7.9$ | $7.03 \mathrm{t} \quad J(\mathrm{HH})=7.7$ |
| H-11 | $7.60 \mathrm{t} \quad J(\mathrm{HH})=7.0$ | $7.50 \mathrm{t} \quad J(\mathrm{HH})=7.6$ | $7.21 \mathrm{t} \quad J(\mathrm{HH})=7.4$ | $6.84 \mathrm{t} \quad J(\mathrm{HH})=7.6$ |
| H-12 | $7.89 \mathrm{~d} J(\mathrm{HH})=6.9$ | $7.75 \mathrm{~d} \quad J(\mathrm{HH})=7.8$ | $7.87 \mathrm{~d} \quad J(\mathrm{HH})=7.3$ | $7.65 \mathrm{~d} \quad J(\mathrm{HH})=8.0$ |
| $\mathrm{NH}_{2}$ |  | 6.00 s, br |  | 7.51 s , br |

${ }^{\text {a }}$ Two phenyl rings in azobenzene and its complexes are equivalent.
${ }^{\mathrm{b}} \mathbf{a z b}=$ azobenzene, ${ }^{\mathrm{c}} \mathbf{a} \mathbf{a z b}=4$-aminoazobenzene.
${ }^{\mathrm{d}}(\mathbf{1})=\{\mathrm{PdCl}(\mathrm{dmf})\}_{2}\left(\mu-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{~N}=\mathrm{NC}_{6} \mathrm{H}_{4}\right),{ }^{\mathrm{e}}(\mathbf{2})=\{\mathrm{PdCl}(\mathrm{dmf})\}_{2}\left(\mu-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{~N}=\mathrm{NC}_{6} \mathrm{H}_{3} \mathrm{NH}_{2}\right)$.
${ }^{\mathrm{f}}$ By dissolving complexes $\mathbf{1}$ and $\mathbf{2}$ in dmso- $\mathrm{d}_{6}$, molecules of $\mathrm{dmf}-\mathrm{h}_{7}$ are replaced with dmso- $\mathrm{d}_{6}$ forming complexes $\mathbf{3}$ and $\mathbf{4}$, respectively. The signals corresponding to free dmf- $\mathrm{h}_{7}$ were observed in the spectra of complexes $\mathbf{1}$ and $\mathbf{2}$.

Table S2. ${ }^{13} \mathrm{C}$ NMR data in DMSO ( $\delta / \mathrm{ppm}$ )

|  | Compound $^{\mathrm{a}}$ |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| $\mathbf{C}$ | $\mathbf{a z b}$ | $\mathbf{a a z b}$ | $\mathbf{1}^{\mathrm{b}} \mathbf{( 3 )}$ | $\mathbf{2}^{\mathrm{b}} \mathbf{( 4 )}$ |
| $\mathbf{C - 1}$ | 152.0 | 142.8 | 143.0 | 149.2 |
| C-2 | 122.16 | 125.0 | 159.0 | 155.3 |
| C-3 | 129.5 | 113.3 | 128.6 | 122.0 |
| C-4 | 131.6 | 152.4 | 126.0 | 153.5 |
| $\mathbf{C - 5}$ | 129.5 | 113.3 | 131.6 | 111.8 |
| C-6 | 122.2 | 125.0 | 136.5 | 131.2 |
| C-7 | 152.0 | 152.7 | 143.0 | 142.7 |
| C-8 | 122.2 | 121.6 | 159.0 | 160.6 |
| C-9 | 129.5 | 129.0 | 128.6 | 122.0 |
| C-10 | 131.6 | 129.2 | 126.0 | 124.8 |
| C-11 | 129.5 | 129.0 | 131.6 | 125.3 |
| C-12 | 122.2 | 121.6 | 136.5 | 135.4 |

${ }^{\text {a }}$ Two phenyl rings in azobenzene and its complexes are equivalent.
${ }^{\mathrm{b}}$ The signals corresponding to free dmf- $\mathrm{h}_{7}$ or $\mathrm{dmso}-\mathrm{h}_{6}$ were also observed in the spectra of complexes.

Table S3. Crystallographic parameters

| Compound | 1 | 4 |
| :---: | :---: | :---: |
| Molecular formula | $\mathrm{C}_{18} \mathrm{H}_{22} \mathrm{Cl}_{2} \mathrm{~N}_{4} \mathrm{O}_{2} \mathrm{Pd}_{2}$ | $\mathrm{C}_{16} \mathrm{H}_{22} \mathrm{Cl}_{2} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{Pd}_{2} \mathrm{~S}_{2}$ |
| $M_{\mathrm{r}}$ | 610.14 | 636.25 |
| $T\left({ }^{\circ} \mathrm{C}\right)$ | 20 | 20 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P 2{ }_{1} / \mathrm{c}$ | $P 2{ }_{1} / \mathrm{c}$ |
| $a / \AA$ | 12.7700(10) | 12.1444(5) |
| $b / \AA$ | 5.2796 (6) | 6.2403(2) |
| $c / \AA$ | 15.4190(8) | 13.8844(7) |
| $\beta /{ }^{\circ}$ | 92.460(10) | 95.021(3) |
| $V / \AA^{3}$ | 1038.60(15) $\AA^{3}$ | 1048.19(8) |
| Z | 2 | 2 |
| $D_{\mathrm{x}} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.951 | 2.016 |
| Crystal colour and form | red needle | red needle |
| Crystal dimensions (mm) | $0.02 \times 0.02 \times 0.12$ | $0.02 \times 0.05 \times 0.12$ |
| $\mu\left(\mathrm{Cu}-K_{\alpha}\right) / \mathrm{mm}^{-1}$ | 16.53 | 18.203 |
| Absorption correction | $\Psi$-scan | $\Psi$-scan |
| Total data | 2271 | 2308 |
| Unique data | 2183 | 2205 |
| Observed data | 1721 | 1691 |
| $R_{\text {int }}$ | 0.0425 | 0.0254 |
| $\theta_{\text {max }} /{ }^{\circ}$ | 76.44 | 76.53 |
| $h k l$ limits | -16,16; 0,6; -19,0 | -15,0; -7,0;-17,17 |
| $R_{1}\left[\mathrm{~F}_{\mathrm{o}}>4 \sigma\left(\mathrm{~F}_{\mathrm{o}}\right)\right]$ | 0.0480 | 0.0415 |
| $w R_{2}\left(\mathrm{~F}^{2}\right)$, all data | 0.1409 | 0.1148 |
| Goodness of fit, $S$ | 1.061 | 1.033 |
| Number of variables | 133 | 129 |

Table S4. Comparison of experimental and calculated bond lengths (in $\AA$ ) around Pd-atom

| 1 |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | X-ray | RHF/B1 ${ }^{\text {a }}$ | B3LYP/B1 ${ }^{\text {a }}$ | RHF/B2 ${ }^{\text {b,c }}$ | B3LYP/B2 ${ }^{\text {b,c }}$ |
| Pd-C | 1.937 | 1.994 | 1.978 | 1.981 | 1.968 |
| Pd-N | 2.067 | 2.216 | 2.102 | 2.240 | 2.128 |
| Pd-O | 2.192 | 2.201 | 2.246 | 2.254 | 2.279 |
| $\mathrm{Pd}-\mathrm{Cl}$ | 2.294 | 2.428 | 2.402 | 2.396 | 2.360 |
| 4 |  |  |  |  |  |
|  | X-ray ${ }^{\text {d }}$ | RHF/B ${ }^{\text {a,d }}$ | B3LYP/B1 ${ }^{\text {a,d }}$ | RHF/B2 ${ }^{\text {b,d }}$ | B3LYP/B2 ${ }^{\text {b,d }}$ |
| Pd-C | 1.952 | 1.998 | 1.981 | 1.984 | 1.967 |
|  |  | 1.996 | 1.983 | 1.981 | 1.969 |
| Pd-N | 2.055 | 2.199 | 2.096 | 2.224 | 2.120 |
|  |  | 2.211 | 2.098 | 2.232 | 2.123 |
| $\mathrm{Pd}-\mathrm{O}$ | 2.178 | 2.177 | 2.194 | 2.228 | 2.248 |
|  |  | 2.187 | 2.209 | 2.240 | 2.267 |
| Pd-Cl | 2.315 | 2.442 | 2.423 | 2.407 | 2.378 |
|  |  | 2.438 | 2.418 | 2.405 | 2.373 |
| $\mathrm{S}=\mathrm{O}$ | 1.524 | 1.685 | 1.722 | 1.521 | 1.550 |
|  |  | 1.686 | 1.722 | 1.521 | 1.550 |
| $\mathrm{C}-\mathrm{NH}_{2}$ | 1.250 | 1.378 | 1.385 | 1.375 | 1.374 |

${ }^{\mathrm{a}} \mathrm{B} 1$ denotes smaller basis set with Los Alamos ECP and DZ basis on $\mathrm{Pd}, \mathrm{S}$ and Cl atoms and D95V basis on all other atoms.
${ }^{\mathrm{b}}$ B2 denotes larger basis set with Los Alamos pseudopotential and DZ basis only on Pd atoms and 6$31 \mathrm{G}(\mathrm{d}, \mathrm{p})$ basis on all other atoms.
${ }^{\text {c }}$ Geometry optimization with $\boldsymbol{C}_{i}$ symmetry yielded one small negative frequency less than $10 \mathrm{~cm}^{-1}$.
${ }^{\mathrm{d}}$ Geometry obtained by X-ray diffraction has pseudo $\boldsymbol{C}_{i}$ symmetry (not really present in the molecule). Calculated distances are shown for both pseudosymmetrical bonds, first for those around Pd -atom linked to aromatic ring with $\mathrm{NH}_{2}$ bond.

Table S5. Calculated energies of all configurational isomers of $\mathbf{3}^{\text {a,b }}$ in Hartrees.

|  | $\mathrm{O}-\mathrm{Pd} / \mathrm{O}-\mathrm{Pd}$ | $\mathrm{O}-\mathrm{Pd} / \mathrm{S}-\mathrm{Pd}$ | $\mathrm{S}-\mathrm{Pd} / \mathrm{O}-\mathrm{Pd}$ | $\mathrm{S}-\mathrm{Pd} / \mathrm{S}-\mathrm{Pd}$ |
| :--- | :--- | :--- | :--- | :--- |
| cis/cis | -2851.6438 | -2851.6386 | - | -2851.6336 |
| cis/trans | -2851.6503 | -2851.6368 | -2851.6455 | -2851.6314 |
| trans/trans | -2851.6583 | -2851.6441 | - | -2851.6296 |

${ }^{\text {a }}$ Rows indicate positions of dmso in respect to Pd-C bonds on two sides of the complex, and columns indicate the heteroatom by which dmso was bound to Pd atom.
${ }^{\mathrm{b}}$ Energies are corrected for zero point of energy (ZPE).

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