

## Electronic Supplementary Information

### **Aggregates of a hetero-oligophenylene derivative as reactors for the generation of palladium nanoparticles: a potential catalyst in the Sonogashira coupling reaction under aerial conditions**

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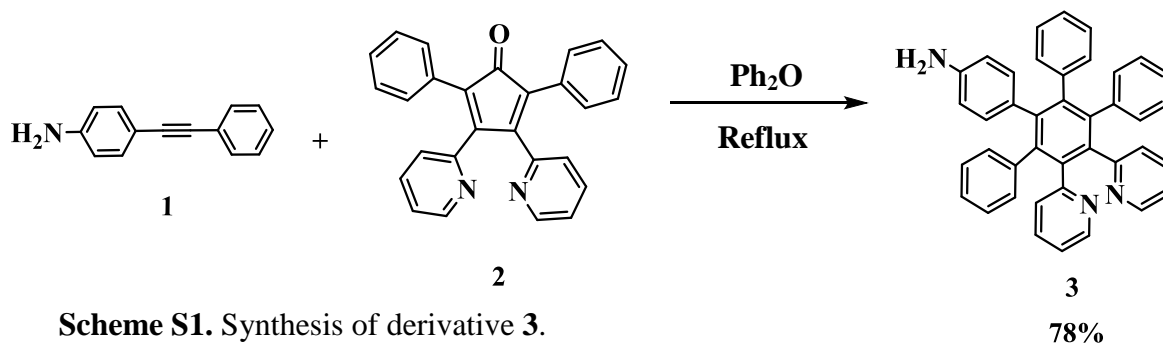
### **General experimental methods:**

All the fluorescence spectra were recorded on SHIMADZU 5301 PC spectrofluorometer. UV spectra were recorded on Shimadzu UV-2450 PC spectrophotometer with a quartz cuvette (path length: 1 cm). The cell holder was thermostated at 25°C. Elemental analysis was done using a Flash EA 1112 CHNS/O analyzer of Thermo Electron Corporation. The dynamic light scattering (DLS) data were recorded with a Malvern Instruments Nano-ZS. The time-resolved fluorescence spectra were recorded with a HORIBA time-resolved fluorescence spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL-FT NMR-AL 300 MHz spectrophotometer, Bruker (Avance II) FT-NMR-AL 500 MHz spectrophotometer using  $\text{CDCl}_3$  as solvent and tetramethylsilane  $[\text{Si}(\text{CH}_3)_4]$  for internal standards. Data are reported as follows: chemical shifts in parts per million ( $\delta$ ), multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), integration, and interpretation. All spectral characterizations were carried out in HPLC grade solvents at 20°C within a 10 mm quartz cell.

### **Procedure for analytes sensing:**

For each experiment we have taken 3 ml solution which contains solution of derivative **3** in 15  $\mu\text{l}$  of THF diluted with 885  $\mu\text{l}$  of EtOH and 2.1 ml HEPES buffer (0.05 M, pH = 7.05) or double distilled water. UV-vis and fluorescence titrations were performed with 5.0  $\mu\text{M}$  solutions of ligand (15  $\mu\text{l}$  of THF are used to dissolve) in  $\text{H}_2\text{O}/\text{EtOH}$  (8:2, v/v). Typically, aliquots of freshly prepared standard solutions ( $10^{-1}\text{M}$  to  $10^{-3}\text{M}$ ) of metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Au}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Li}^+$  as their chloride/perchlorate salts. In titration experiments, each time a 3 ml solution of **3** was filled in a quartz cuvette (path length, 1 cm) and spectra were recorded.

+



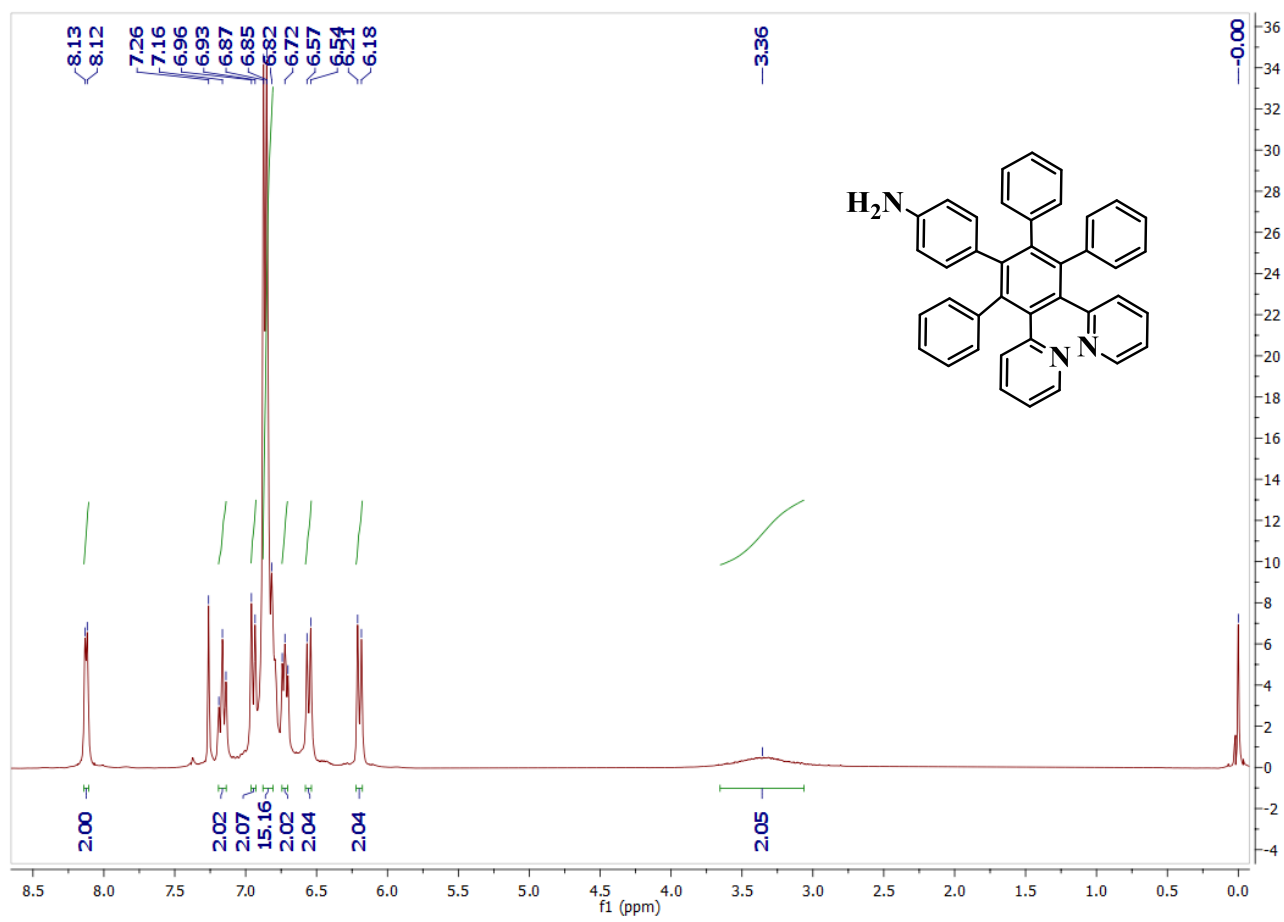
**Synthesis of Compound (3):** A solution of 4-Phenylethynyl-phenylamine **1** (0.20 g, 1.0 mmol) and 2,5-diphenyl-3,4-di(pyridin-2-yl)cyclopenta-2,4-dienone **2** (0.40 g, 1.0 mmol) in 2 mL of diphenylether was refluxed for 24 h under an inert atmosphere. After the completion of the reaction, the reaction mixture was cooled to room temperature followed by addition of 10 ml cold methanol to the reaction mixture and kept for stirring. The dark brown solid separates out and the solid were filtered as residue. The brown solid was subjected to column chromatography using 7:3 CHCl<sub>3</sub>/hexane as the eluent. The compound was recrystallized from methanol to give **3** as a light yellow solid. Yield=78%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.12 (d, *J* = 3Hz, 2H), 7.16 (t, *J* = 7.5Hz, 2H), 6.95 (d, *J* = 9Hz, 2H), 6.87-6.82 (m, 15H, ArH), 6.72 (t, *J* = 6Hz, 2H), 6.55 (d, *J* = 9Hz, 2H), 6.20 (d, *J* = 9Hz, 2H), 3.36 (brs, 2H, NH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm) δ = 147.7, 134.3, 132.2, 131.4, 131.2, 126.7, 126.6, 125.4, 125.3, 125.2, 120.1, 113.8. ESI-MS *m/z*: 552.6176 [M+H]<sup>+</sup>, calculated for C<sub>40</sub>H<sub>29</sub>N<sub>3</sub>. Elemental analysis: Calculated for C<sub>40</sub>H<sub>29</sub>N<sub>3</sub>: C 87.08; H 5.30; N 7.62; Found: C 87.07%; H 5.28%; N 7.65.

**Table S1:** Comparison of present method over other reported procedure in literature for the preparation of palladium nanoparticles.

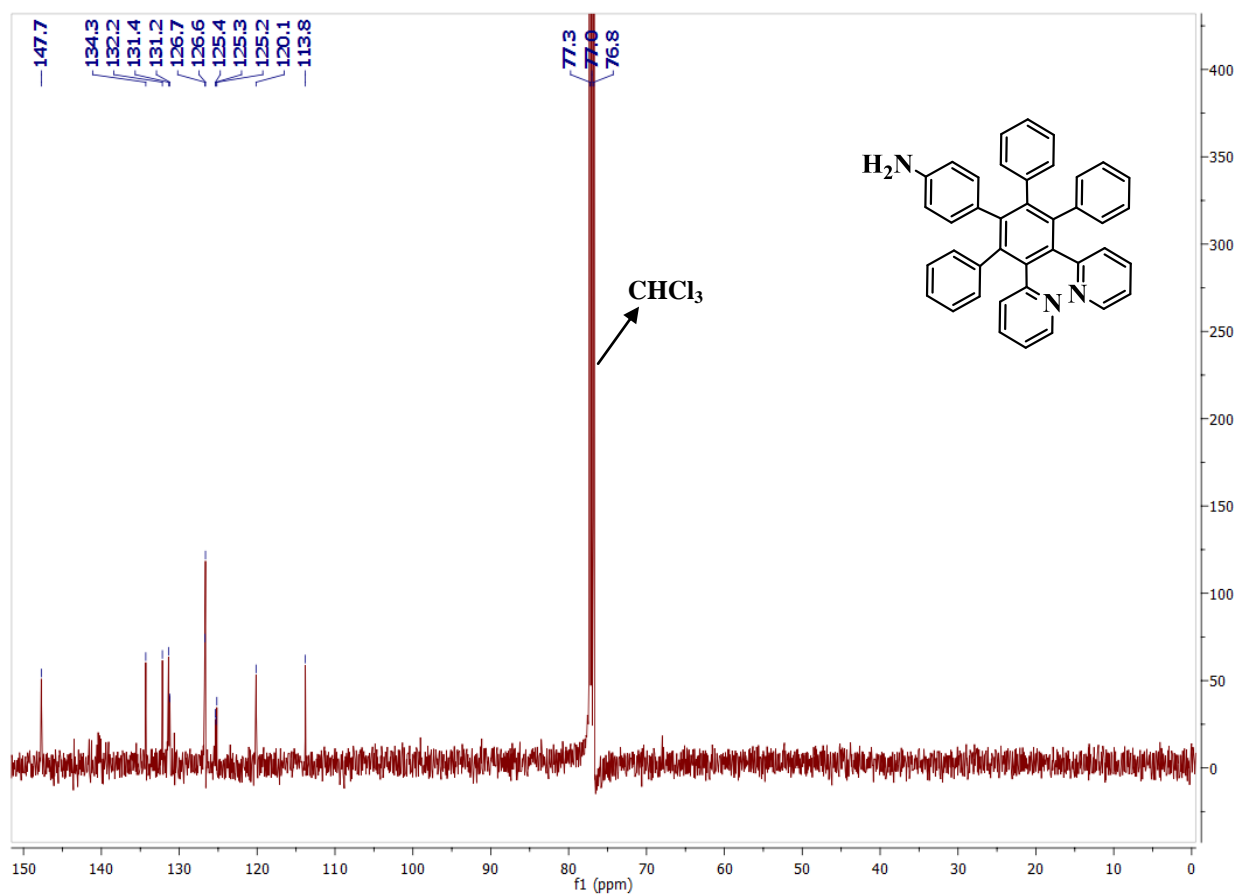
| Entry | Method of formation of palladium nanoparticles | Size of palladium nanoparticles | Reaction time to prepare palladium nanoparticles | Reducing agent or surfactants or stabilizers                                | Reaction temp. (°C) | Nanoparticles  | Journals  |
|-------|--|---------------------------------|--|---|---------------------|--|---|
| 1     | Wet Chemical Method                            | 5.6 nm (average)                | 10 mins  | No  | Room Temp.          | Palladium Nanoparticles (Pd NPs)   | Present Manuscript  |
| 2     | Chemical Method                                | 10 nm                           | 3 hrs  | yes   | 80 °C               | Palladium Nanocubes (PdNC)   | <i>ACS Applied Materials &amp; Interfaces</i> , 2015<br>DOI:<br>10.1021/am509124x |
| 3     | Chemical Method                                | 3.7 nm (average)                | 8.5 hrs  | sodium citrate( stabilizing agent) and NaBH <sub>4</sub> ( reductive agent) | 0 °C to 60 °C       | carbon-supported Pd NPs  | <i>J. Am. Chem. Soc.</i> , 2015, <b>137</b> , 4288.                               |
| 4     | Chemical Method                                | 3-5 nm                          | 4 hrs  | Et <sub>4</sub> NBr   | 4 hrs               | (Pd NPs)   | <i>Org. Lett.</i> 2015, <b>17</b> , 1770.   |
| 5     | Mechanical Method                              | -----                           | 10 mins  | no  | Room Temp.          | [Pd(II) nanoparticles on multiwalled carbon nanotubes, Pd(II)/MWCNT  | <i>Org. Lett.</i> 2015, <b>17</b> , 1782.   |
| 6     | Chemical Method                                | 10 nm (average)                 | overnight  | N,N-bisimine ligand   | 80 <sup>0</sup> C   | nano tetraimine Pd(0) complex  | <i>Green Chemistry</i> , 2015<br>DOI:<br>10.1039/c5gc00616c                       |
| 7     | Chemical Method                                | between 5 and 10 nm             | 13 hrs   | end-capped B-BO <sub>3</sub>  | 90 <sup>0</sup> C   | Pd@B-BO <sub>3</sub>   | <i>Chem. Mater.</i> , 2015, <b>27</b> , 1921.                                     |
| 8     | Chemical Method                                | 29.3 nm                         | 4 hrs  | H <sub>2</sub> PdCl <sub>4</sub> /HCl                                       | 500 °C              | mesoporous silica-supported Pd and PdO NPs   | <i>Chem. Mater.</i> , 2015, <b>27</b> , 29.                                       |
| 9     | Carbonyl-mediated method                       | -----                           | 25 mins  | FeCl <sub>3</sub> (oxidative etching agent)                                 | Room Temp.          | Pd nanowires   | <i>J. Am. Chem. Soc.</i> , 2014, <b>136</b> , 12856.                              |
| 10    | Chemical Method                                | -----                           | 3.5 hrs  | NaBH <sub>4</sub>   | Room Temp           | Pd-binaphthyl nanoparticles/Pd- <i>p</i> -decylphenyl nanoparticles/Pd- <i>p</i> -decyloxyphenyl nanoparticles/Pd-phenyl nanoparticles | <i>Org. Lett.</i> , 2014, <b>16</b> , 3856.                                       |
| 11    | Chemical Method                                | 2.97 nm. (average)              | 6 hrs  | dicarboxylic acids  | 70 <sup>0</sup> C   | Pd@HPS-N(C <sub>12</sub> H <sub>25</sub> ) <sup>3+</sup> Cl <sup>-</sup> on cotton and filter papers                                   | <i>Adv. Synth. Catal.</i> 2014, <b>356</b> , 951.                                 |

**Table S2:** Comparison of catalytic efficiency of generated Pd NPs for palladium catalyzed Sonogashira cross coupling reaction in present manuscript with literature Reports.

| Entry | Reaction                   | Solvent                     | Base  | Time          | Catalyst                                | Temp. (°C) | Yield (%) | References   |
|-------|----------------------------|-----------------------------|---|---------------|---|------------|-----------|--|
| 1     | Sonogashira cross-coupling | H <sub>2</sub> O/EtOH (7:3) | K <sub>2</sub> CO <sub>3</sub>                    | 10 to 55 mins | Pd NPs                                  | r.t. to 90 | 96        | Present manuscript   |
| 2     | Sonogashira cross-coupling | H <sub>2</sub> O            | (i-Pr) <sub>2</sub> NH                            | 24h           | Pd supp. Over polyimides                | 100        | 88-100    | <i>Green Chem.</i> , 2015, <b>17</b> , 466                   |
| 3     | Sonogashira cross-coupling | DMF                         | KOH   | 1h            | Cu/Pd deposited on graphene oxide       | 120        | 95        | <i>ACS Appl. Mater. Interfaces</i> , 2015, <b>7</b> , 3199.  |
| 4     | Sonogashira cross-coupling | Isopropanol                 | K <sub>2</sub> CO <sub>3</sub>                    | 7h            | Pd-complex from Schiff base             | RT         | 98        | <i>New J. Chem</i><br>DOI:<br>10.1039/c4nj01822b             |
| 5     | Sonogashira cross-coupling | Solvent free                | Piperidine  | 2h            | SBA16 supported heterogeneous Pdcomplex | 80         | 94        | <i>New J. Chem.</i><br>DOI:<br>10.1039/c4nj02319f            |
| 6     | Sonogashira cross-coupling | Solvent free                | Et <sub>3</sub> N                                 | 2h            | palladium NHC complex with a space      | 90         | 95        | <i>New J. Chem.</i> , 2015, <b>39</b> , 2333.                |
| 7     | Sonogashira cross-coupling | DMF/ H <sub>2</sub> O       | K <sub>2</sub> CO <sub>3</sub>                    | 3h            | Pd/MIL-101                              | 130        | 50        | <i>Appl. Organometal. Chem.</i> , 2015, <b>29</b> , 234.     |
| 8     | Sonogashira cross-coupling | DMF                         | NEt <sub>3</sub>                                  | 12h           | PdCl <sub>2</sub>                       | 65         | 100       | <i>Org.Lett.</i> , 2014, <b>16</b> , 5024.                   |
| 9     | Sonogashira cross-coupling | EtOH                        | K <sub>2</sub> CO <sub>3</sub> , PPh <sub>3</sub> | 16h           | Pd                                      | 65         | 32        | <i>ACS Appl. Mater. Interfaces</i> , 2014, <b>6</b> , 20261. |
| 10    | Sonogashira cross-coupling | CH <sub>3</sub> CN,DBMP     | IPr NHC   | 12h           | Pd/Au                                   | 25         | 70-80     | <i>Org. Process Res. Dev.</i> , 2014, <b>18</b> , 1786.      |
| 11    | Sonogashira cross-coupling | NMP                         | KOAc  | -----         | Pd nanoparticles                        | 135        | 73-99     | <i>Angew.Chem.Int. Ed.</i> , 2013, <b>52</b> , 11554.        |
| 12    | Sonogashira cross-coupling | H <sub>2</sub> O            | hexamine  | 10-14h        | Pd-LHMS-3                               | 120        | 85        | <i>Green Chem.</i> , 2012, <b>14</b> , 2840.                 |

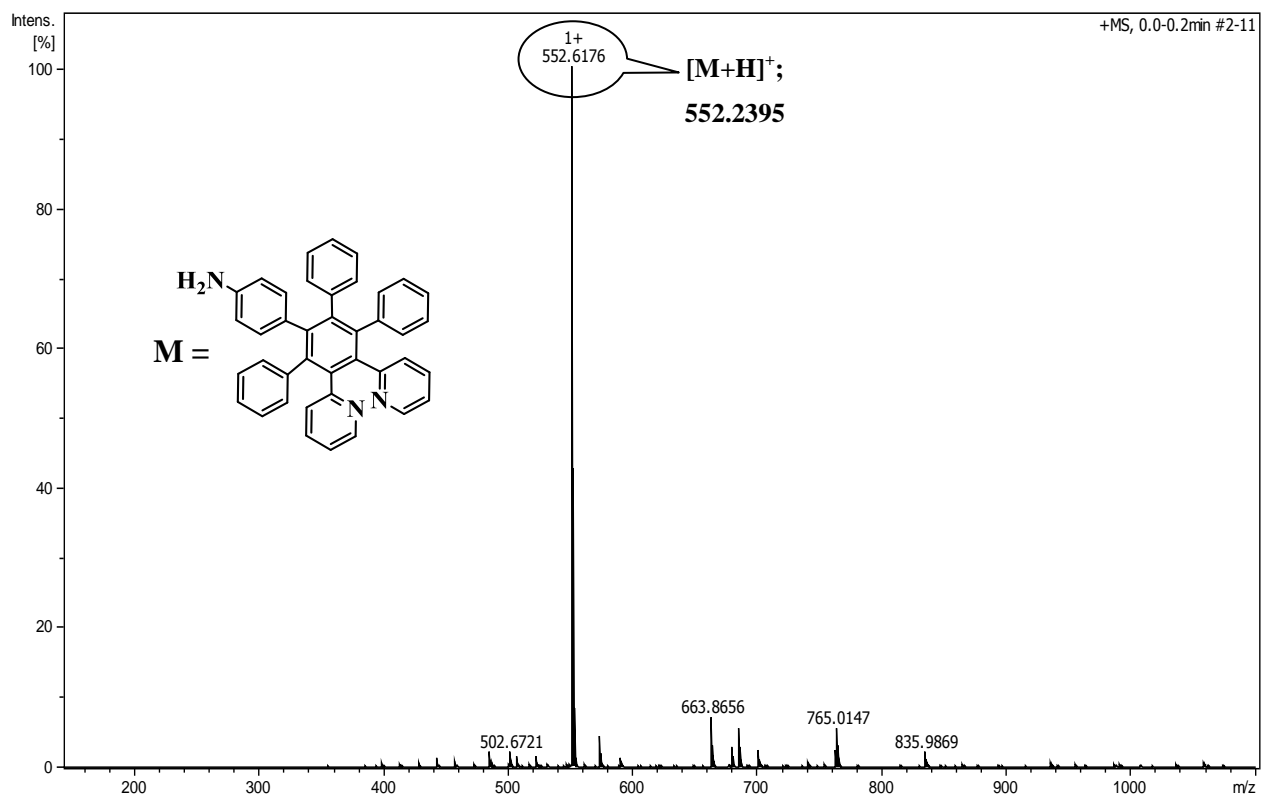


**Fig. S1**  $^1\text{H}$  NMR Spectra ( $\text{CDCl}_3$ , 300 MHz, ppm) of compound **3**.

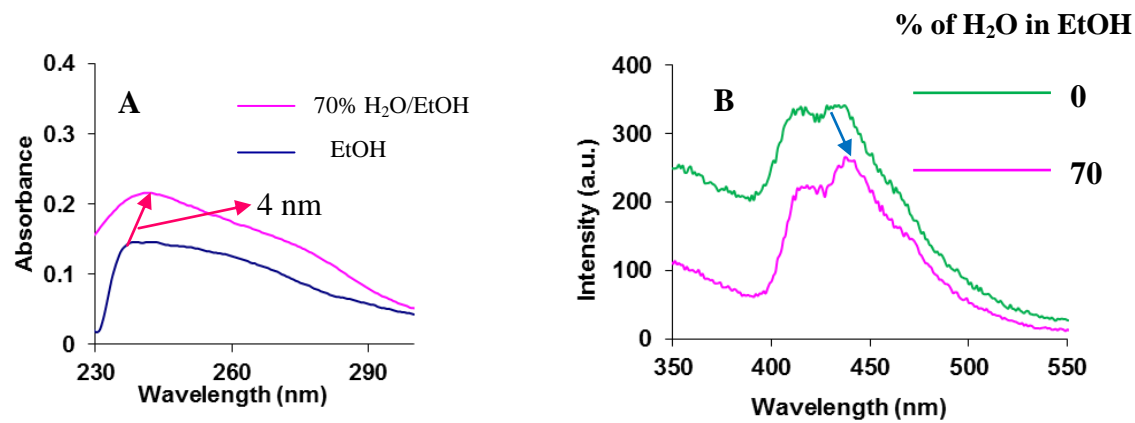


**Fig. S2**  $^{13}\text{C}$  NMR Spectra ( $\text{CDCl}_3$ , 125 MHz, ppm) of compound **3**.

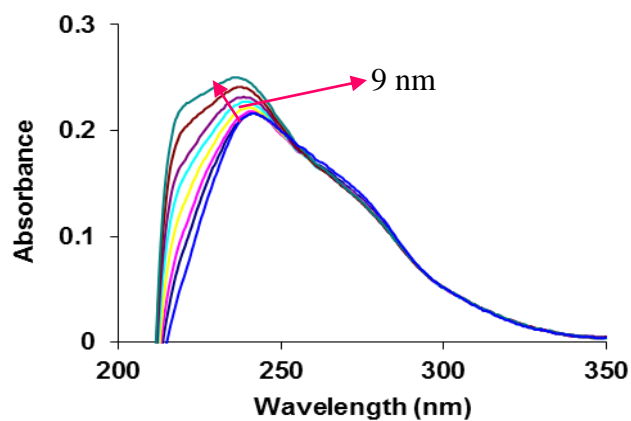




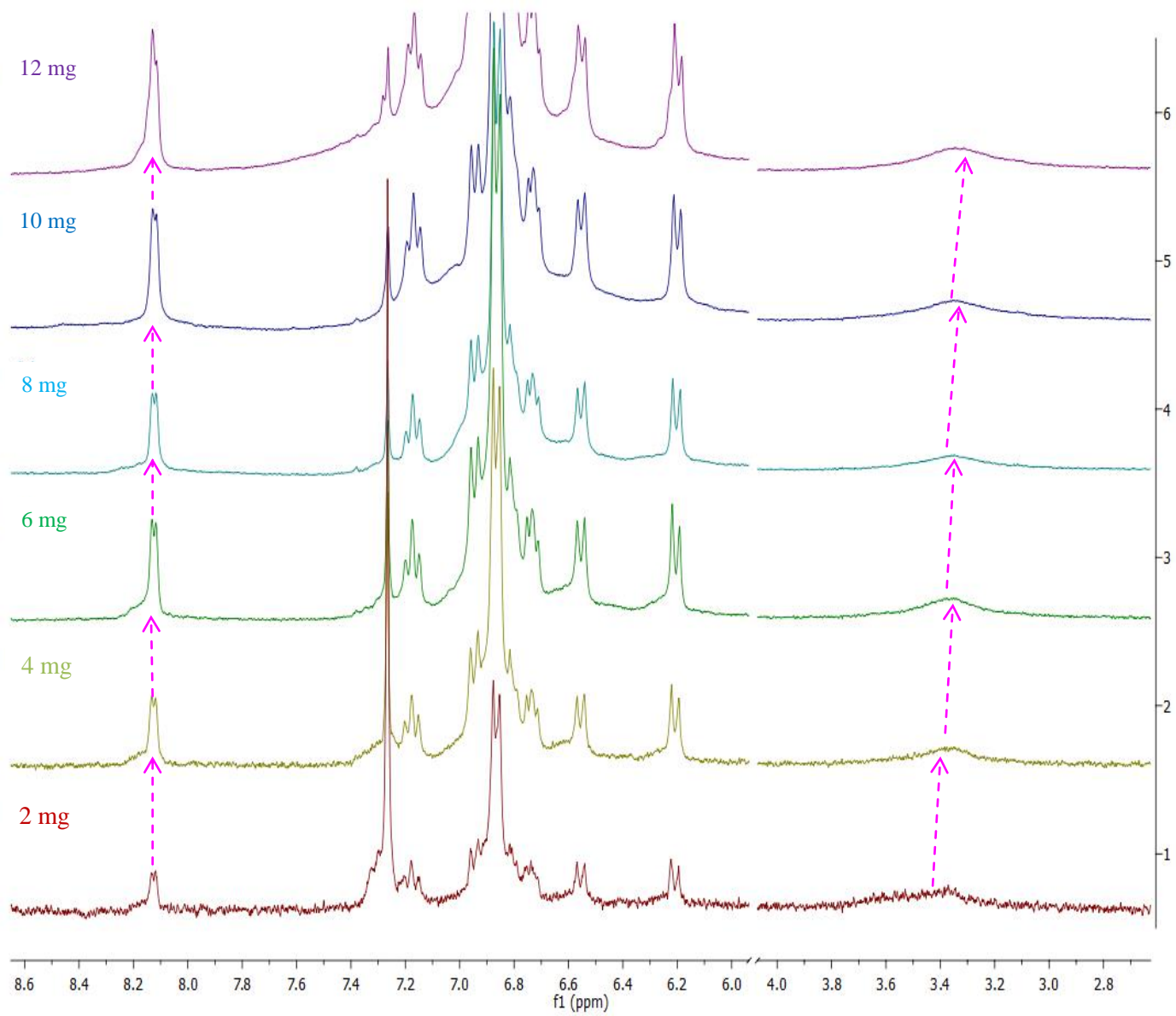
**Fig. S3** Mass Spectrum (ESI-MS) of compound **3**.



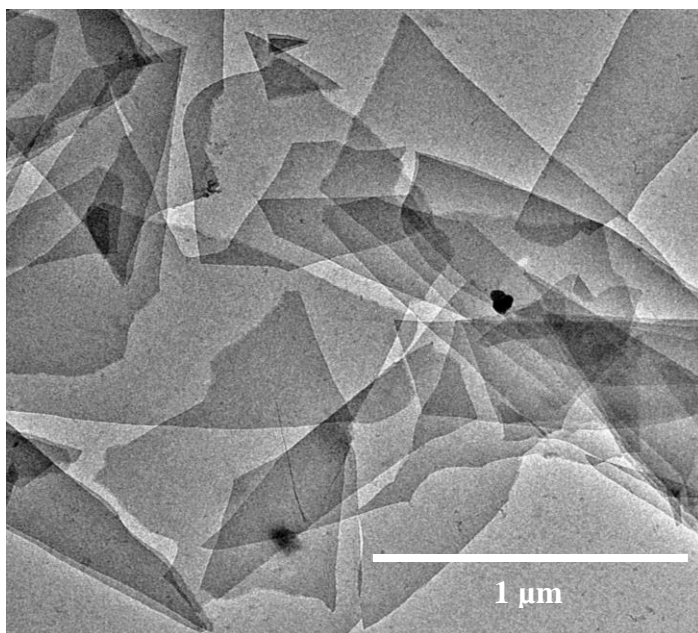
**Fig. S4** (A) UV-vis spectra of derivative **3** (5  $\mu\text{M}$ ) showing the variation of absorbance in EtOH and Bathochromic shift of the absorption band upon addition of water (70% volume fractions) to the EtOH solution of compound **3**; (B) Fluorescence emission spectra of derivative **3** in EtOH and H<sub>2</sub>O/EtOH (7:3) at  $\lambda_{\text{ex}} = 270 \text{ nm}$ .



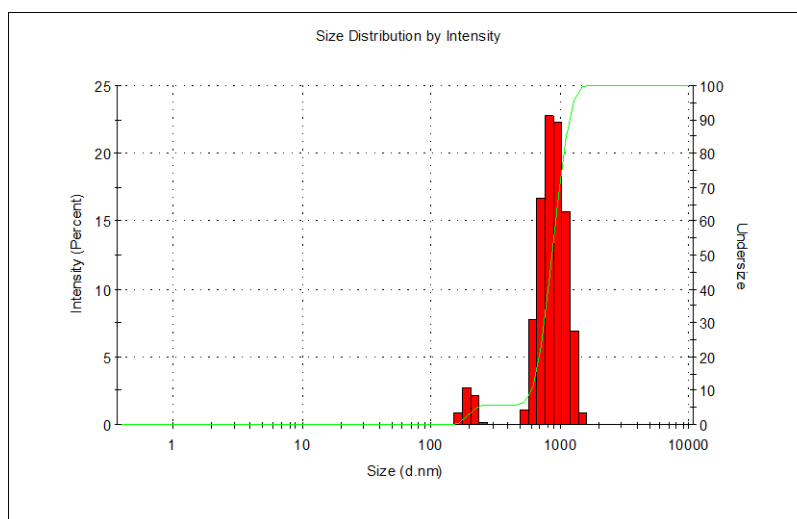
**Fig. S5** Temperature-dependent (25°C to 70°C) UV-vis studies of aggregates of derivative **3** in H<sub>2</sub>O/EtOH (7:3) solvent mixture.



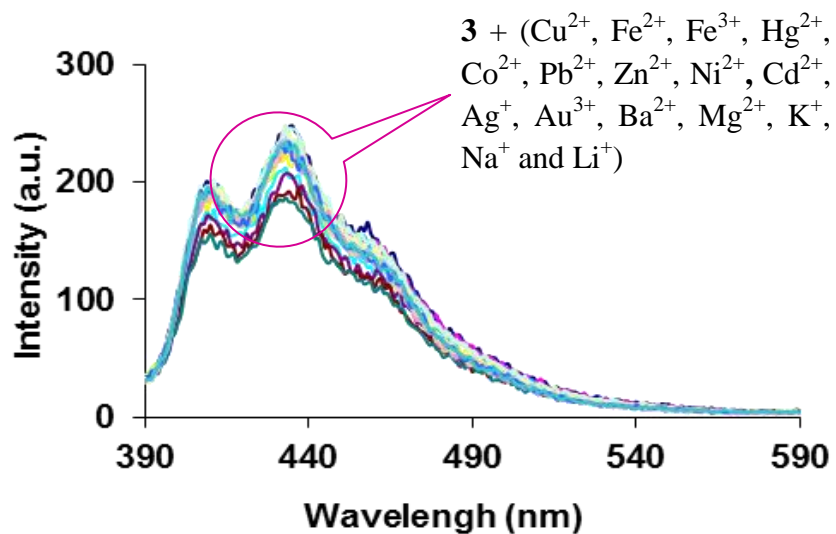
**Fig. S6** Concentration dependent  $^1\text{H}$  NMR spectra of derivative **3** in  $\text{CDCl}_3$ .



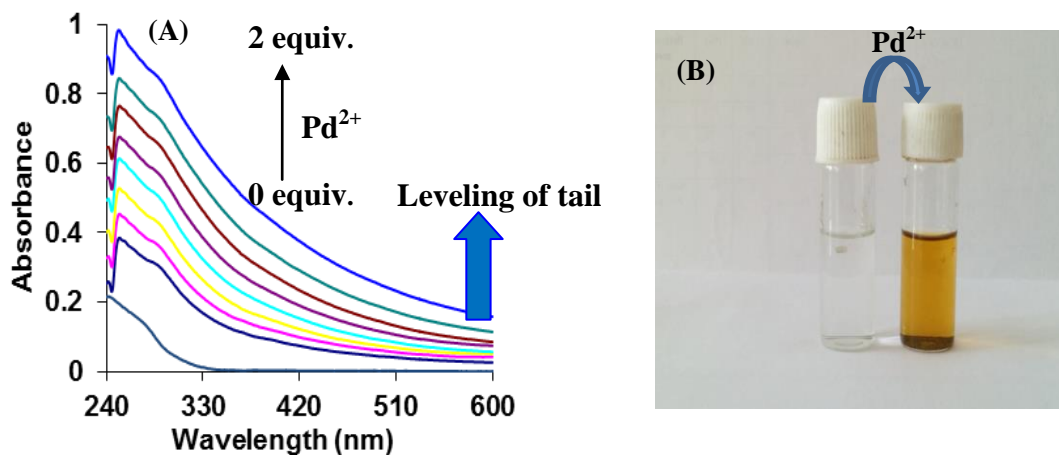
**Fig. S7** Transmission electronic microscopy (TEM) image of derivative **3** in H<sub>2</sub>O/EtOH (7:3) mixture.



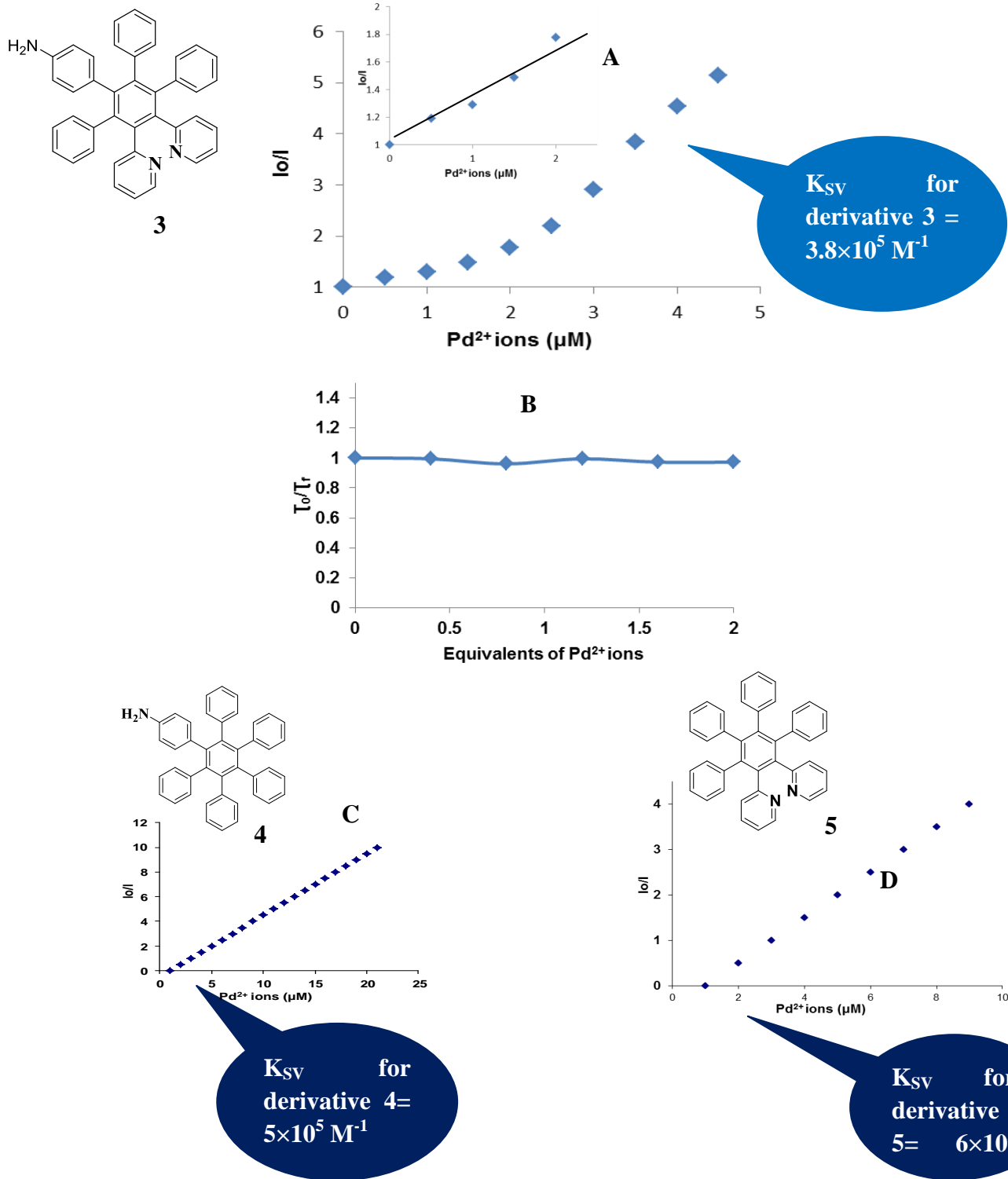
**Fig. S8** The dynamic light scattering (DLS) studies derivative **3** showing the average diameter of aggregates is in the range of 900 nm in H<sub>2</sub>O/EtOH (7:3).



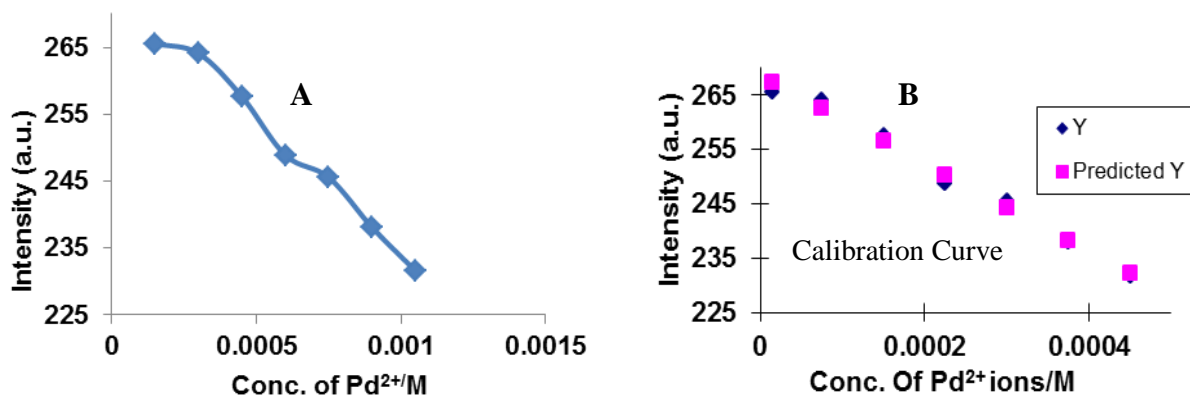
**Fig. S9** Change in the fluorescence spectra of compound **3** (5 μM) upon additions of metal perchlorates/chloride (5 μM) in H<sub>2</sub>O/EtOH (7:3) buffered with HEPES, pH = 7.05.



**Fig. S10** (A) UV-vis spectrum of compound **3** (5 μM) upon addition of 2 equiv. of Pd<sup>2+</sup> ions in H<sub>2</sub>O/EtOH (7:3). (B) Chromogenic behaviour of aggregates of derivative **3** towards Pd<sup>2+</sup> ions with a color change from colorless to brown that is clearly visible to naked eye.



**Fig. S11** Variation of fluorescence intensity ratio ( $I_0/I$ ) of (A) aggregates of derivative 3 (5  $\mu\text{M}$ ) at 440 nm, inset showing the linear Stern-Volmer plot at lower concentration (2.5  $\mu\text{M}$ ); (B) Time resolved fluorescence showing the average life time ratio of derivative 3 in the presence of different concentrations of  $\text{Pd}^{2+}$  ions; (C) aggregates of derivative 4 (5  $\mu\text{M}$ ); (D) aggregates of derivative 5 (5  $\mu\text{M}$ ) in  $\text{H}_2\text{O}/\text{EtOH}$  (7:3, v/v) buffered with HEPES, pH =7.05 in the presence of different concentrations of  $\text{Pd}^{2+}$  ions ( $I_0/I$ ;  $I_0$  = initial fluorescence intensity;  $I$  = Final fluorescence intensity after the addition of  $\text{Pd}^{2+}$  ions).



Multiple R = 0.99187,

R<sup>2</sup> = 0.983806,

Standard deviation = 0.009,

Observation = 7,

Intercept = 273.9033,

Slope = 39519

The detection limit was calculated based on the fluorescence titration. To determine the S/N ratio, the emission intensity of receptor **3** without Pd<sup>2+</sup> was measured by 7 times and the standard deviation of blank measurements was determined. The detection limit is then calculated with the following equation:

$$DL = 3 \times SD/S$$

Where SD is the standard deviation of the blank solution measured by 7 times; S is the slope of the calibration curve.

**From the graph we get slope**

S = **39519**, and SD value is 0.009

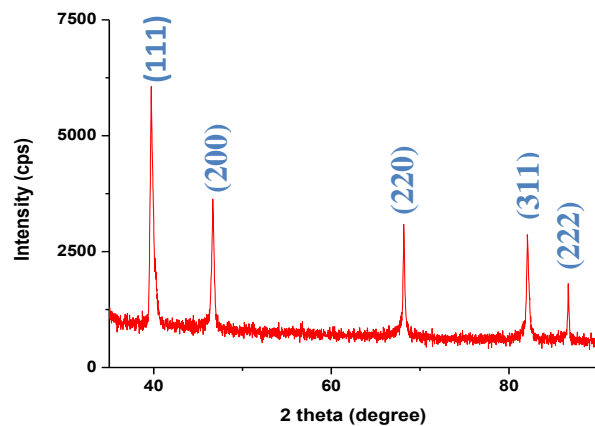
Thus using the formula we get the Detection Limit

$$(DL) = 3 \times 0.009/39519 = 6.83 \times 10^{-7} \text{ M} = 683 \text{ nM}$$

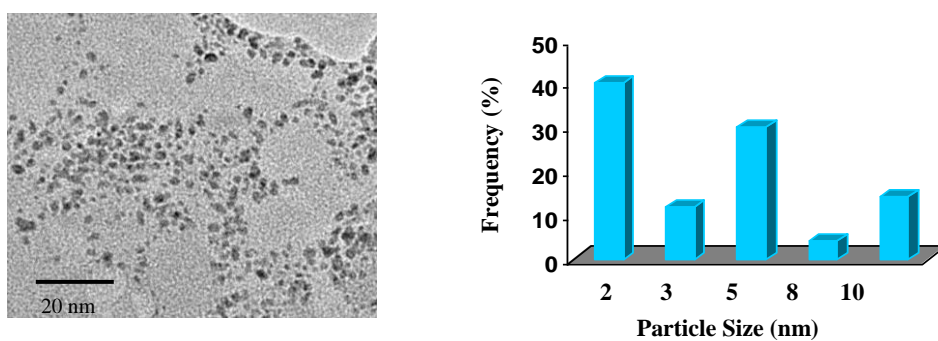
*i.e.*, probe **3** can detect Pd<sup>2+</sup> ions in this minimum concentration through fluorescence method.

**Reference:** S. Goswami, S. Das, K. Aich, D. Sarkar, T. M. Kumar, C. K. Quah and H. K. Fun, *Dalton Trans.*, 2013, **42**, 15113.

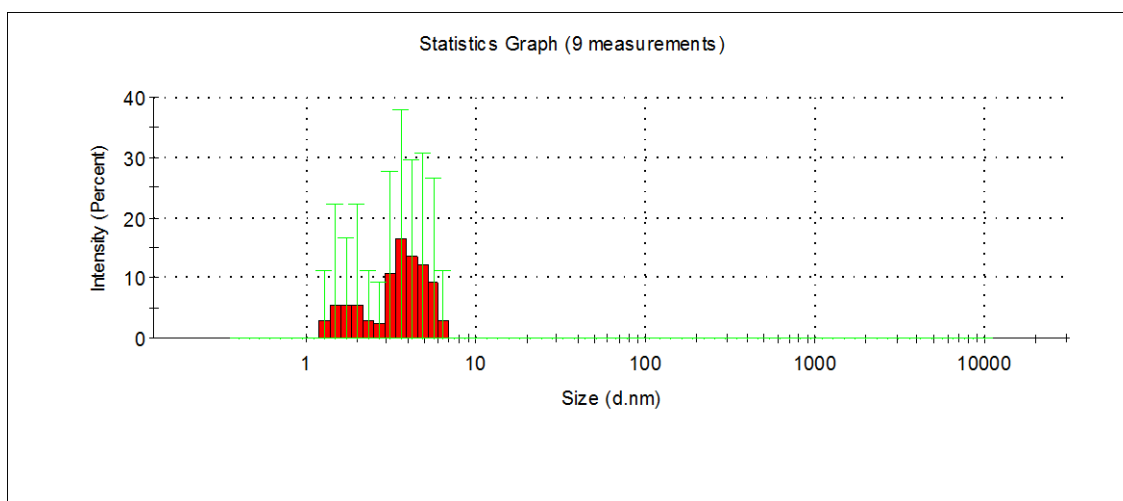
**Fig. S12** (A) Showing the fluorescence intensity of compound **3** and (B) Calibrated curve showing the fluorescence intensity of compound **3** at 437 nm as a function of Pd<sup>2+</sup> ions concentration (equiv.) in H<sub>2</sub>O/EtOH (7:3, v/v) buffered with HEPES, pH =7.05, λ<sub>ex</sub>= 270 nm.



**Fig. S13** Standard XRD analysis of the palladium (0) nanoparticles.

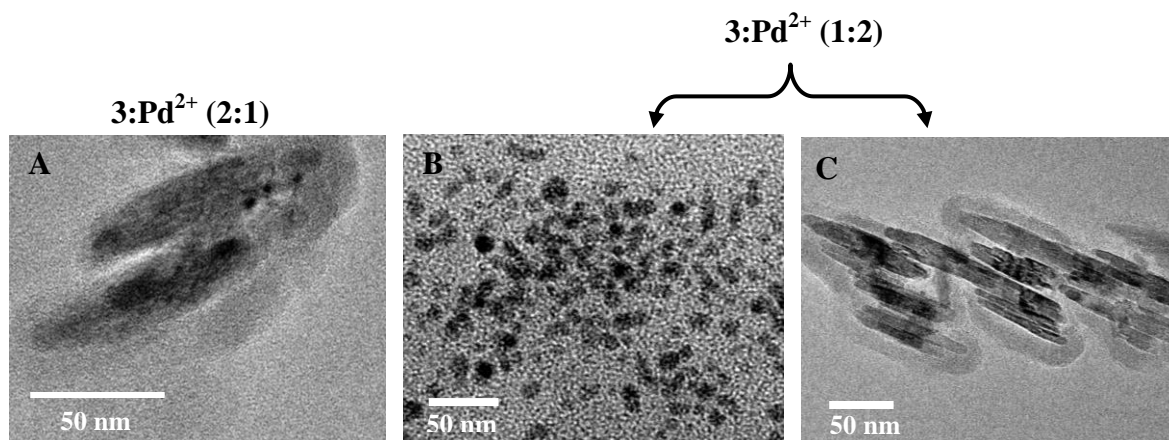


**Fig. S14** TEM image of spherical palladium nanoparticles generated from the aggregates of derivative **3** in the ratio 1:1. The right side of this image shows the respective particle size distribution histogram.

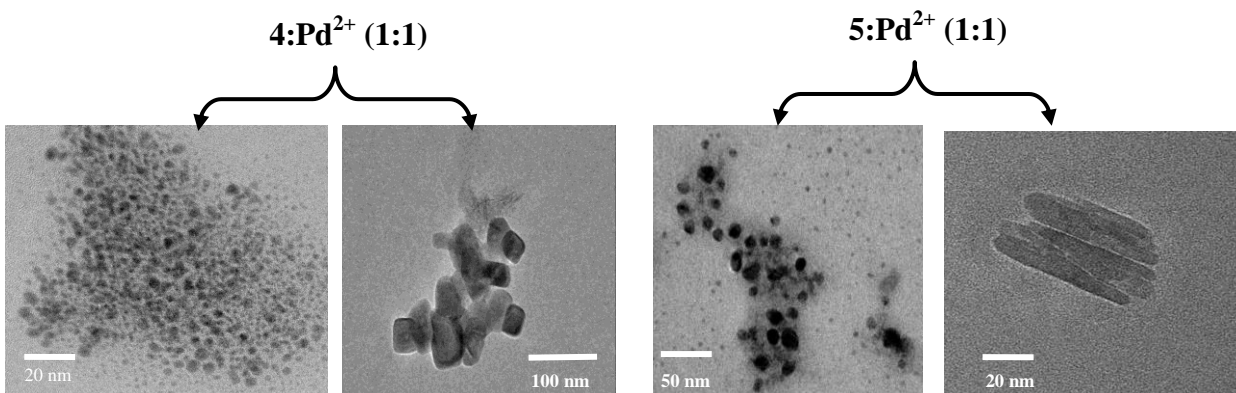


**Fig. S15** The dynamic light scattering (DLS) studies of derivative **3** in presence of 2 equiv. of  $\text{Pd}^{2+}$  ions, showing the average diameter of palladium nanoparticles 7 nm.

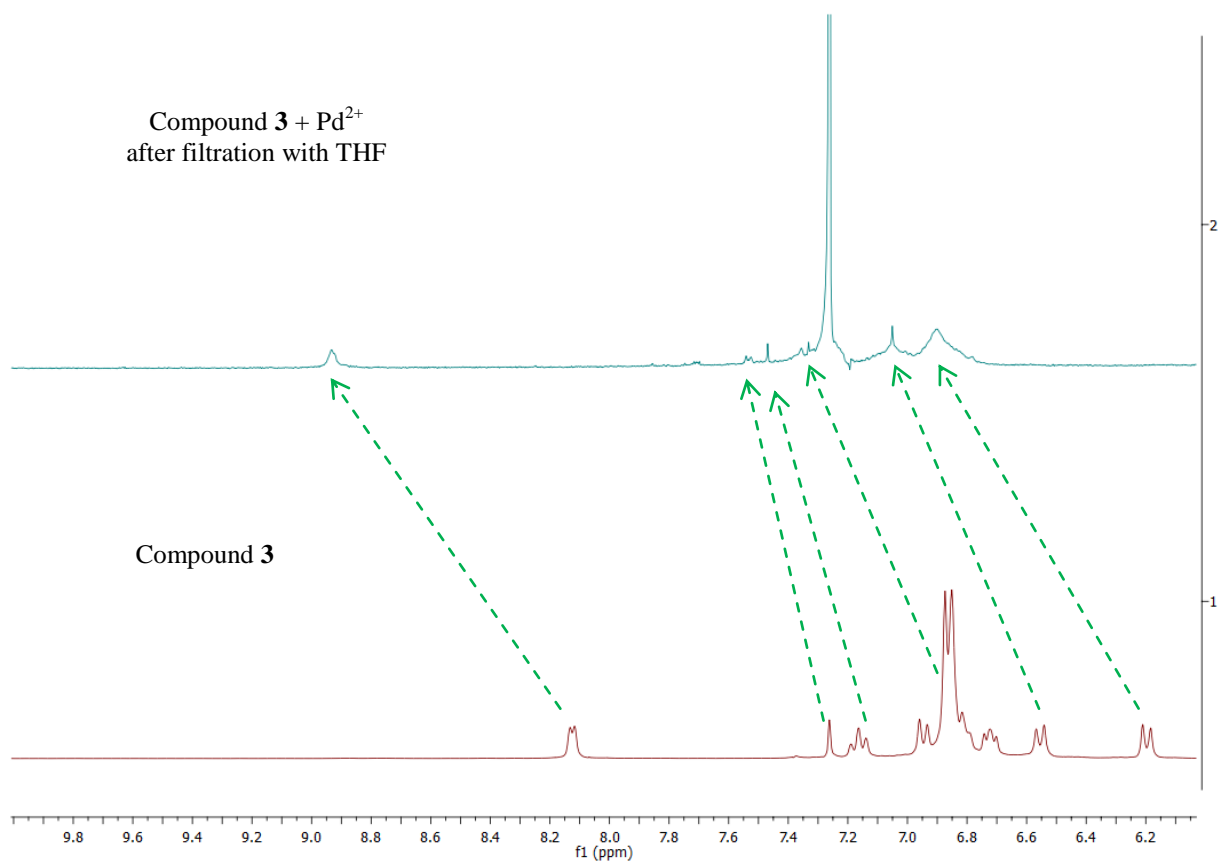




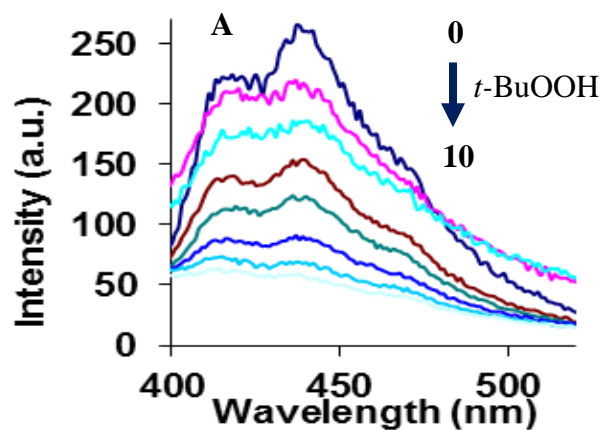
**Fig. S16** (A) TEM image of spherical palladium nanoparticles generated from the aggregates of derivative 3 in the ratio of aggregates of derivative 3 to that  $\text{Pd}^{2+}$  ions 2:1 (nanorods) while switching this ratio to 1:2 (B) nanospheres and (C) nanorods were observed.



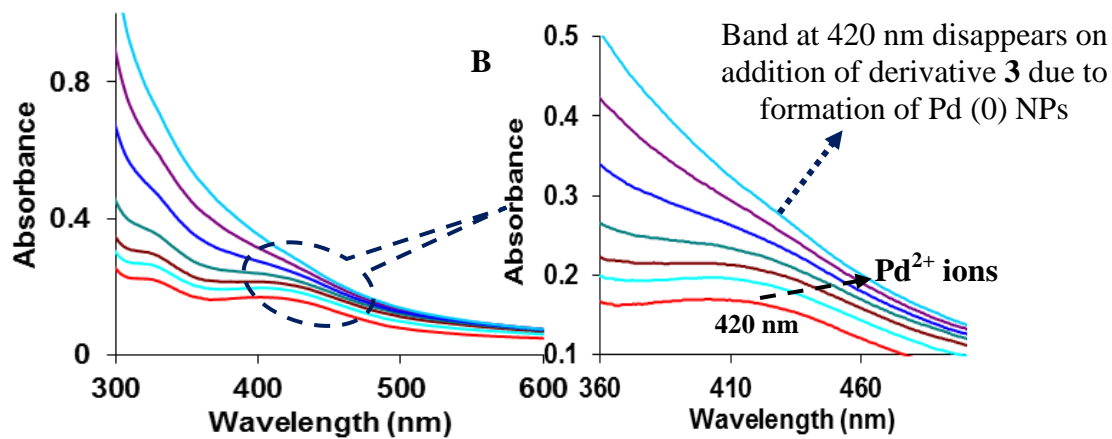
**Fig. S17** (A) and (B) TEM images (nanospheres and nanocubes) of derivative 4 (C) and (D) TEM images (nanospheres and nanorods) of derivative 5.



**Fig. S18** Overlay <sup>1</sup>H NMR spectra of derivative **3** (red) and derivative **3** in presence of Pd<sup>2+</sup> ion followed by filtration with THF and CHCl<sub>3</sub> (Blue).



**Fig. S19(A)** Fluorescence emission spectra of derivative **3** (5  $\mu\text{M}$ ) upon additions of 10 equiv. of *tert*-butyl hydroperoxide solution in  $\text{H}_2\text{O}/\text{EtOH}$  (7:3) mixture.

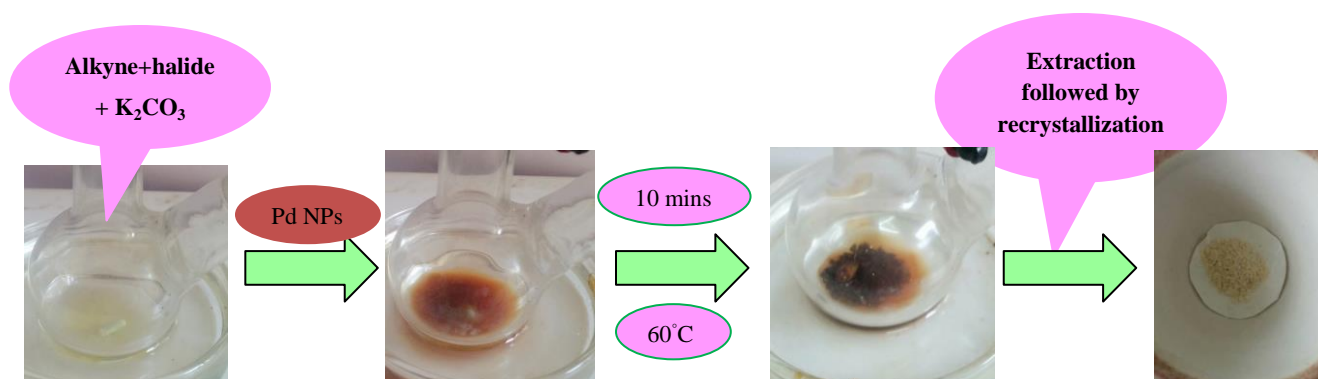


**Fig. S19(B)** UV-visible spectra of  $\text{Pd}^{2+}$  ions and on addition of aggregates of derivative **3** in  $\text{H}_2\text{O}/\text{EtOH}$  (7:3) mixture.

### Sonogashira cross-coupling reaction (procedure and $^1\text{H}$ NMR of final products):

**Synthesis of palladium Nanoparticles.** 600  $\mu\text{l}$  of derivative **3** (1 M) was added 600  $\mu\text{l}$  of 1 M solution of  $\text{PdCl}_2$  in  $\text{H}_2\text{O}/\text{EtOH}$  (7:3, v/v). The reaction was stirred at room temperature for 10 mins and formation of nanoparticles take place. These nanoparticles solution (50  $\mu\text{l}$ ) was used as such in the catalytic experiment.

**General procedure for the Pd NPs catalyzed Sonogashira cross-coupling reaction:** A two-neck 25 ml round bottom flask is charged with solution of 1 mmol of alkyne, 1 mmol of halide, 1 mmol of  $\text{K}_2\text{CO}_3$  and 1 mole % of nano catalyst (Pd NPs) in  $\text{H}_2\text{O}/\text{EtOH}$  (v/v, 7:3) solvent system. The reaction mixture is stirred during 10 to 50 mins at  $\text{rt}/60^\circ\text{C}$ . The final product was isolated by simple extraction with organic solvent and recrystallized to get the pure product.



**Fig. S20** Depiction of the model reaction for Scheme 3 in  $\text{H}_2\text{O}/\text{EtOH}$  (7:3).

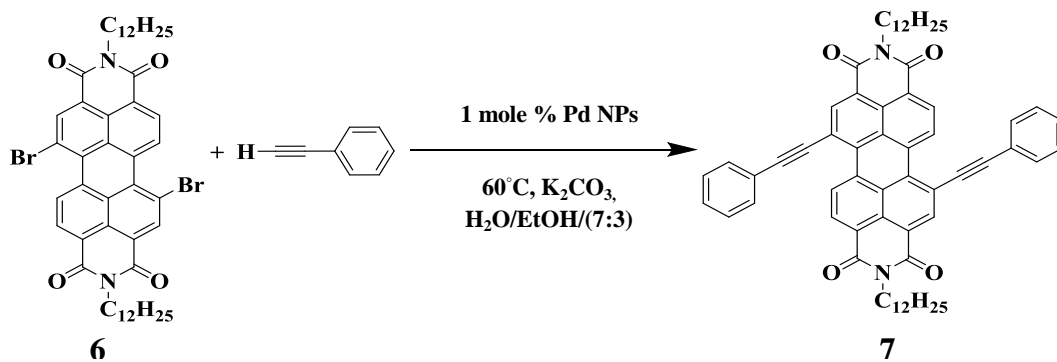
### A typical procedure for the catalyst-recyclability sequence in the Pd NPs-catalyzed Sonogashira cross-coupling reaction:

Further, recyclability of Pd NP catalyst was also checked by monitoring the model reaction between aryl iodide and phenylacetylene. A two neck round bottom flask was charged with 1 mmol of alkyne, 1 mmol of halide and 1 mmol of  $\text{K}_2\text{CO}_3$  and 1 mole % Pd NPs were added as a catalyst in  $\text{H}_2\text{O}/\text{EtOH}$  (7:3) solvent system. The reaction mixture was stirred during 10 mins at  $60^\circ\text{C}$ . The product was separated from the reaction mixture by extracting with organic solvent and the catalyst was recovered in the aqueous layer which was used as such in the next cycle of the reaction. The product yield remained

quantitative even after four cycles of the reaction which indicates that nano catalyst (Pd NPs) have high catalytic activity and stability in our experimental conditions.

**Pd NPs catalyzed ‘Sonogashira cross-coupling’ reaction between Iodobenzene and Phenyl Acetylene Using Various Amounts of Pd NPs:** A 25 ml two-neck round bottom flask is charged with solution with 1mmol of phenyl acetylene, 1 mmol of iodobenzene, 1 mmol of  $K_2CO_3$  and (1-0.0003 mol %) of nano catalyst (Pd NPs) in  $H_2O/EtOH$  (v/v, 7:3) solvent system. The reaction mixture is stirred during 10 mins to 15 h at  $60^\circ C$ . The final product was isolated by simple extraction with organic solvent followed by recrystallization.

**Synthesis of Compound (7).** A 25 ml round bottom flask is charged with 1 mmole of dibromoperylene-diisimide **6**, 2 mmol of phenylacetylene, 1 mmol of  $K_2CO_3$  and 1 mole % of nano catalyst (Pd NPs) in  $H_2O/EtOH$  (7:3) solvent system at  $60^\circ C$  for 12 h to furnish the desired product **7** in 86% yield. The desired product was isolated by simple extraction with organic solvent followed by recrystallization.



**Scheme S2.** Sonogashira coupling of dibromo-perylenebisimide **6** with phenyl acetylene catalyzed by *in situ* generated Pd(0) nanoparticles.

### Characterization Data:

**Compound 10:** The structure of compound **10** was confirmed from its spectroscopic data (Fig. S21, ESI<sup>+</sup>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.54 (d,  $J$  = 5Hz, 2H), 7.52 (d,  $J$  = 5Hz, 2H), 7.34-7.33 (m, 6H).

**Compound 13:** The structure of compound **13** was confirmed from its spectroscopic data (Fig. S22, ESI<sup>+</sup>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.50 (d,  $J$  = 15Hz, 2H), 7.35 -7.30 (m, 5H, ArH), 6.64(d,  $J$  = 10Hz, 2H), 3.82 (brs, 2H, NH<sub>2</sub>).

**Compound 15:** The structure of compound **15** was confirmed from its spectroscopic data (Fig. S23, ESI<sup>+</sup>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 8.23 (d,  $J$  = 10Hz, 2H), 7.68 (d,  $J$  = 5Hz, 2H), 7.58 -7.56 (m, 2H, ArH), 7.41-7.39 (m, 3H, ArH).

**Compound 18:** The structure of compound **18** was confirmed from its spectroscopic data (Fig. S24, ESI<sup>+</sup>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.50-7.48 (m, 4H, ArH), 7.40-7.37 (m, 4H, ArH).

**Compound 20:** The structure of compound **20** was confirmed from its spectroscopic data (Fig. S25, ESI<sup>+</sup>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.31(dd,  $J$  = 5Hz, 2H), 7.28 (dd,  $J$  = 5Hz, 2H), 7.02 (dd,  $J$  = 5Hz, 2H).

**Compound 22:** The structure of compound **22** was confirmed from its spectroscopic data (Fig. S26, ESI<sup>+</sup>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 8.65(d,  $J$  = 10Hz, 2H), 7.73-7.62 (m, 2H, ArH), 7.49-7.43 (m, 2H, ArH), 7.33-7.29(m, 2H, ArH).

**Compound 28:** The structure of compound **28** was confirmed from its spectroscopic data (Fig. S27, ESI<sup>+</sup>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.54-7.48 (m, 4H, ArH), 7.40-7.35 (m, 5H, ArH).

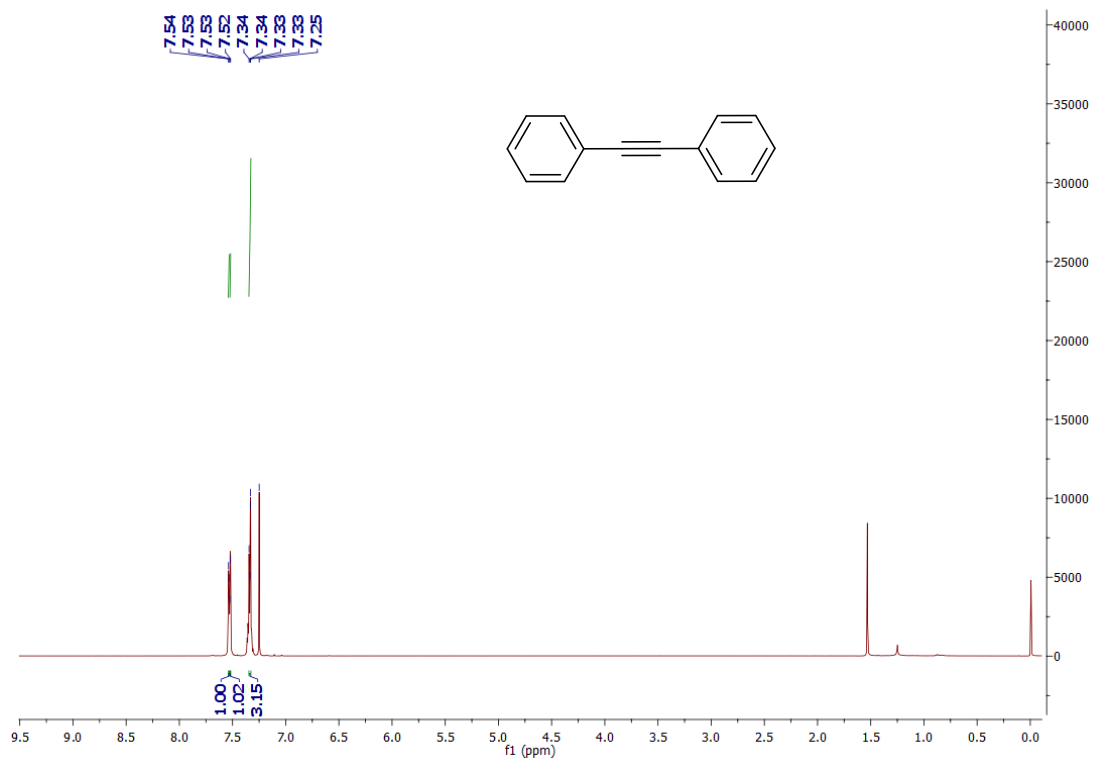


Fig. S21 <sup>1</sup>H NMR Spectra (CDCl<sub>3</sub>, 500 MHz, ppm) of compound 10.

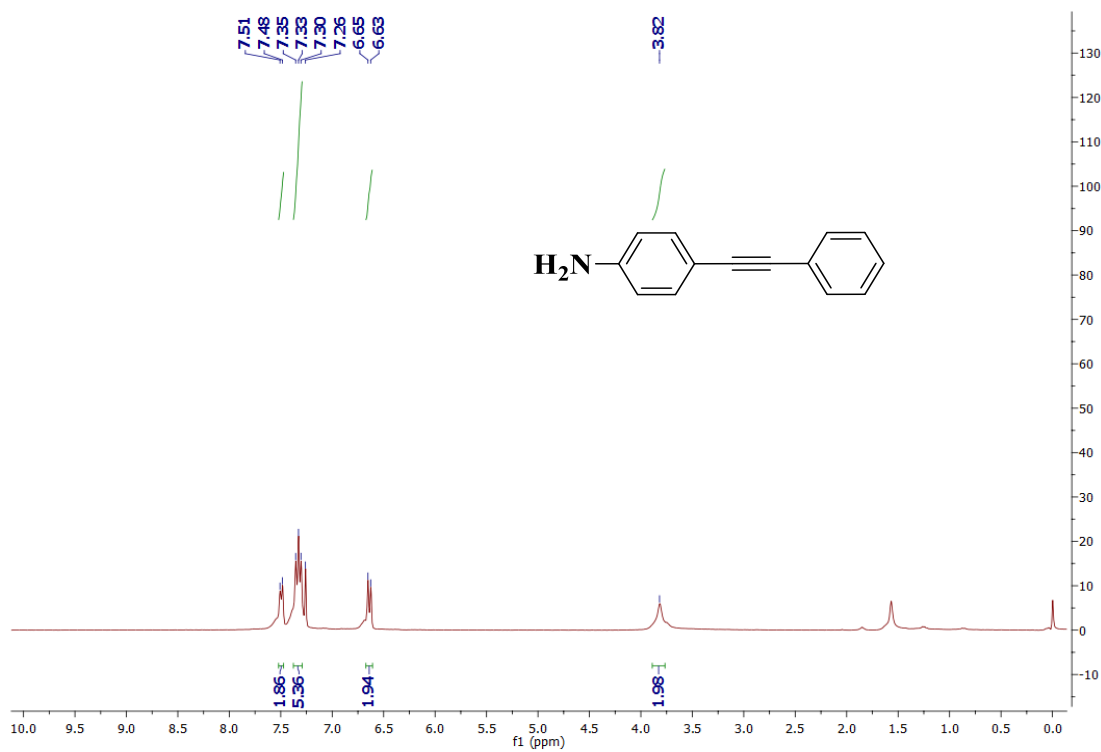


Fig. S22 <sup>1</sup>H NMR Spectra (CDCl<sub>3</sub>, 500 MHz, ppm) of compound 13.

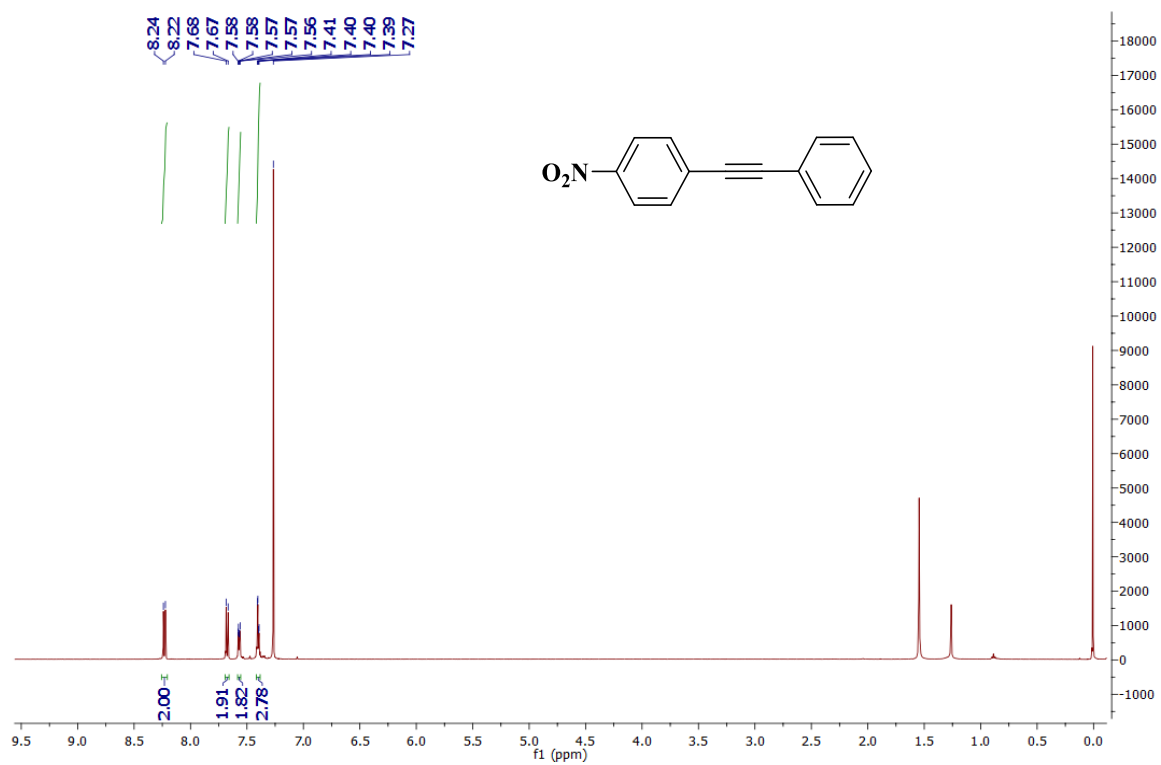


Fig. S23  $^1\text{H}$  NMR Spectra ( $\text{CDCl}_3$ , 500 MHz, ppm) of compound 15.

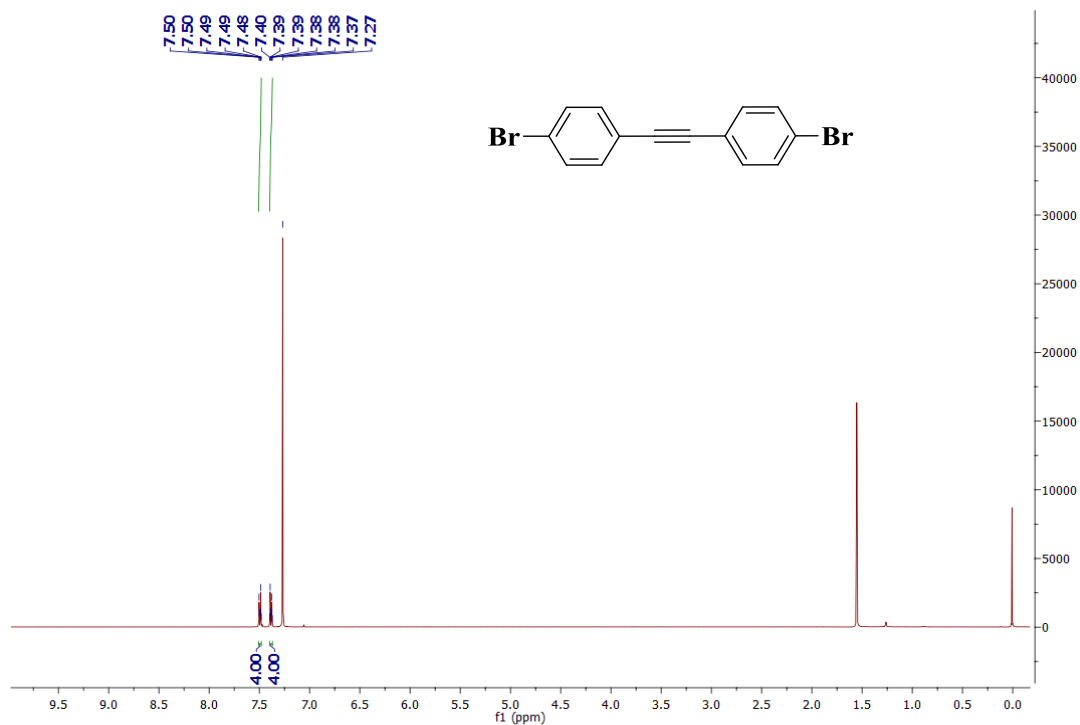


Fig. S24  $^1\text{H}$  NMR Spectra ( $\text{CDCl}_3$ , 500 MHz, ppm) of compound 18.



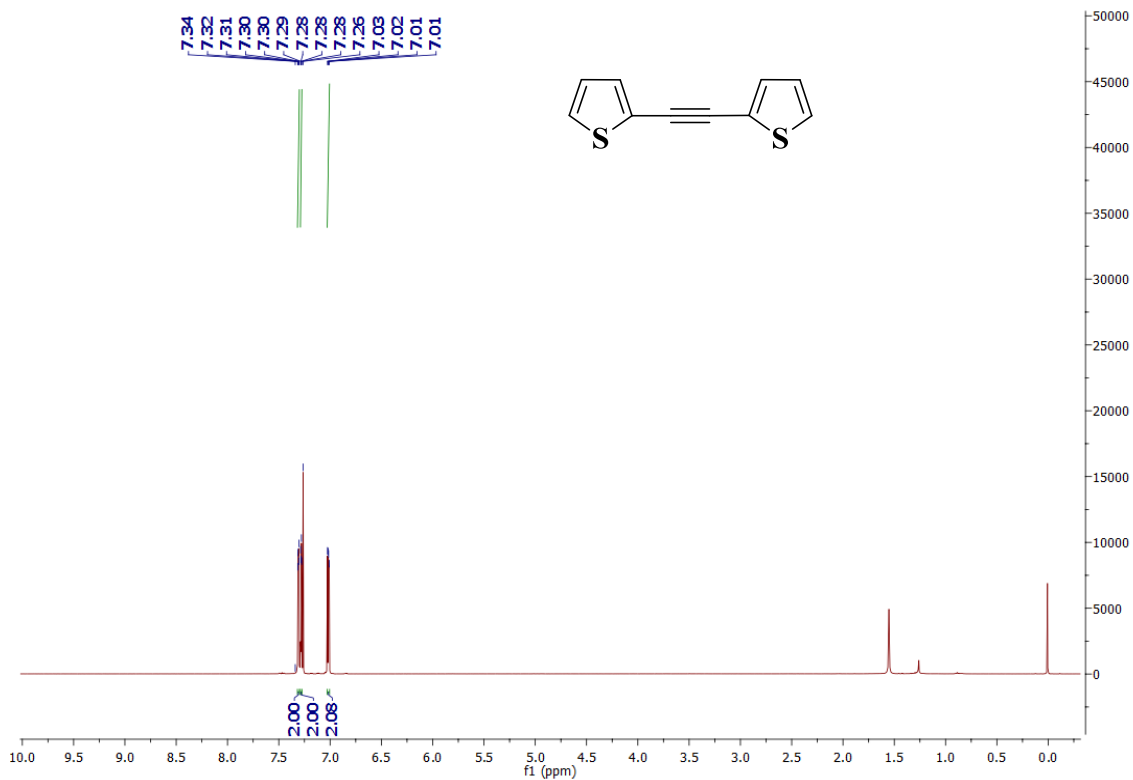


Fig. S25 <sup>1</sup>H NMR Spectra (CDCl<sub>3</sub>, 500 MHz, ppm) of compound 20.

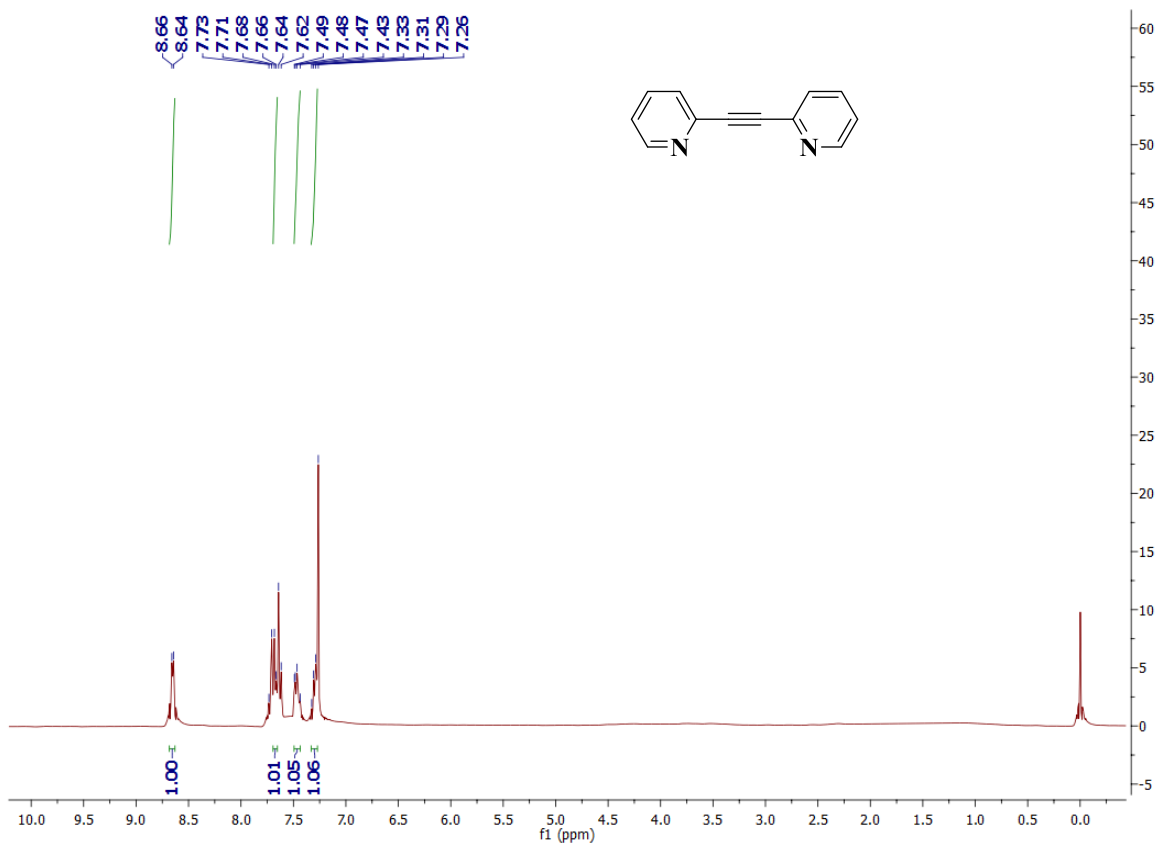


Fig. S26 <sup>1</sup>H NMR Spectra (CDCl<sub>3</sub>, 500 MHz, ppm) of compound 22.

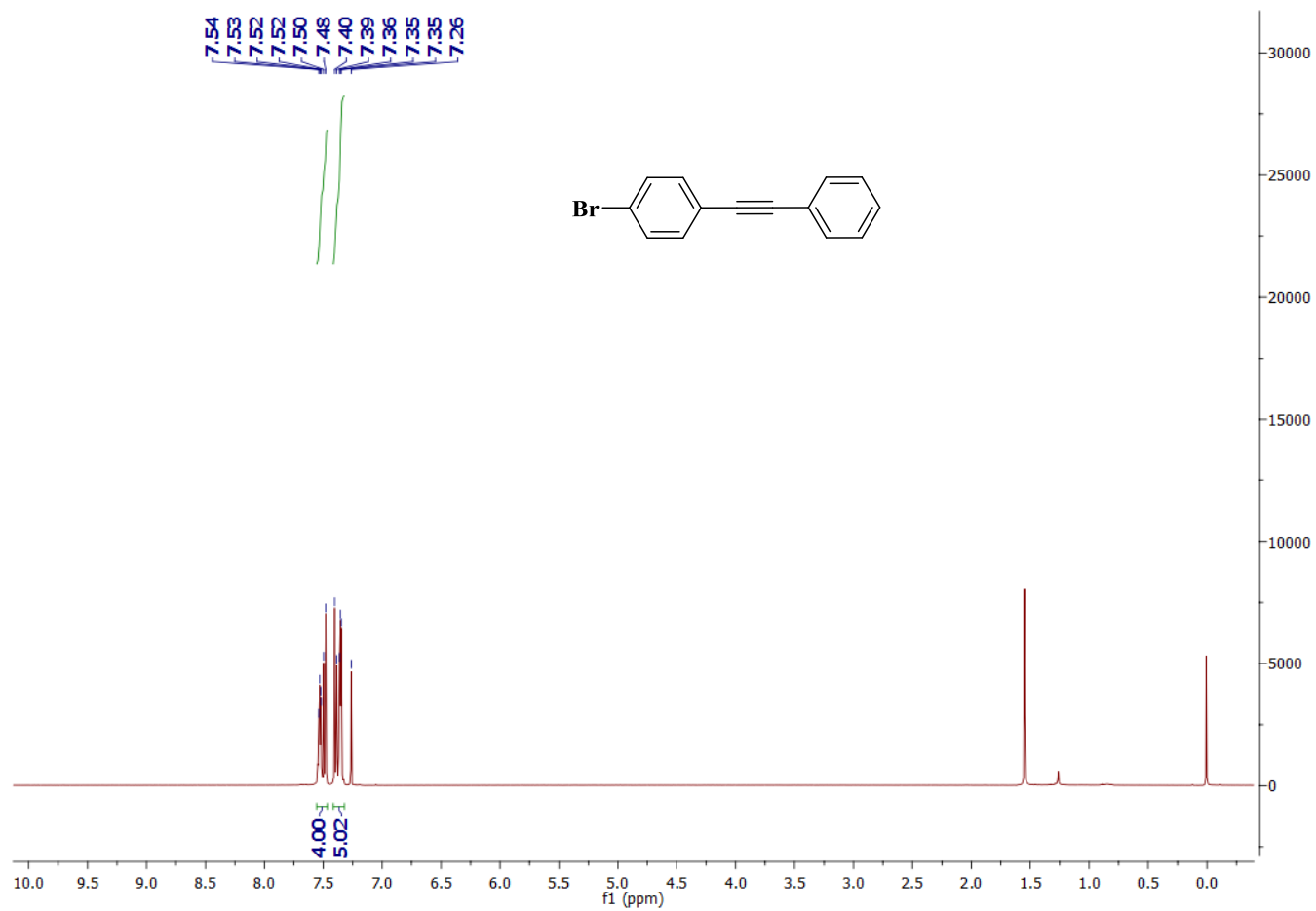
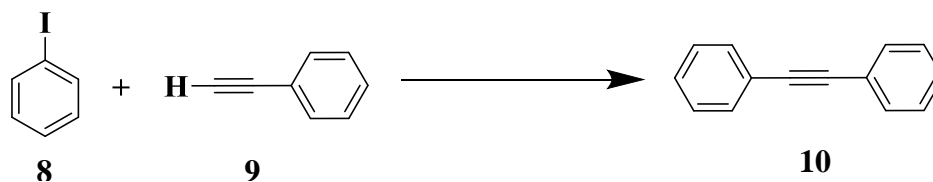


Fig. S27 <sup>1</sup>H NMR Spectra (CDCl<sub>3</sub>, 500 MHz, ppm) of compound 28.



**Scheme S3:** Sonogashira coupling of phenyl acetylene with iodobenzene catalyzed by *in situ* generated Pd(0) nanoparticles.

**Table S3:** Sonogashira coupling of phenylacetylene with iodobenzene by varying the amount of base used and in different solvent media catalyzed by *in situ* generated Pd (0) nanoparticles as shown in Scheme S3.

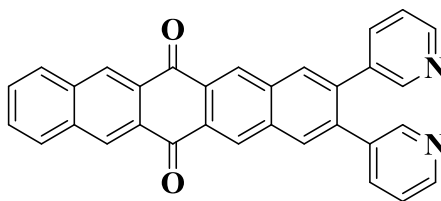
| Entry | Solvent                        | Time (min) | Temp.(°C) | mM of base (K <sub>2</sub> CO <sub>3</sub> ) used | Yield <sup>b</sup> (%) |
|-------|--------------------------------|------------|-----------|---|------------------------|
| 1     | H <sub>2</sub> O               | 50         | RT        | 1   | 98 <sup>a</sup>        |
| 2     | EtOH                           | 50         | RT        | 1   | 94 <sup>a</sup>        |
| 3     | H <sub>2</sub> O/EtOH<br>(7:3) | 50         | RT        | 1   | 96 <sup>a</sup>        |
| 4     | Neat                           | 60         | RT        | 1   | 92 <sup>a</sup>        |
| 5     | H <sub>2</sub> O/EtOH<br>(7:3) | 10         | 60        | 1   | 96 <sup>a</sup>        |
| 6     | DMF                            | 50         | 100       | 1   | 92 <sup>a</sup>        |
| 7     | Toluene                        | 55         | 110       | 1   | 72 <sup>a</sup>        |
| 8     | H <sub>2</sub> O/EtOH<br>(7:3) | 10         | 60        | 2   | 96 <sup>a</sup>        |
| 9     | H <sub>2</sub> O/EtOH<br>(7:3) | 10         | 60        | 4   | 96 <sup>a</sup>        |
| 10    | H <sub>2</sub> O/EtOH<br>(7:3) | 10         | 60        | No Base   | No Reaction            |

<sup>a</sup>under aerial conditions. <sup>b</sup>Isolated yields determined after recrystallization.

**Table S4:** Sonogashira coupling of phenyl acetylene with iodobenzene stabilized by aggregates of derivatives **3**, **4**, **5**, **11** and also only in the presence of Pd<sup>2+</sup> ions as shown in Scheme S3.

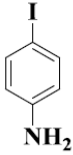
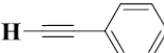
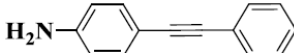
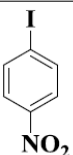
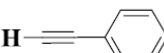
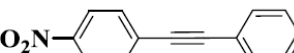
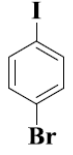

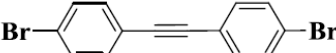
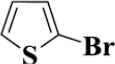

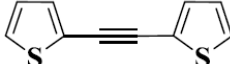
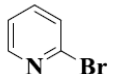

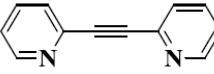
| Entry | Time (min)  | Temp. (°C) | Yield <sup>b</sup> (%) | Pd NPs Of derivative used  |
|-------|-------------|------------|------------------------|--|
| 1     | 50 mins     | RT         | 96 <sup>a</sup>        | 3  |
| 2     | 2 hrs       | 60         | 86 <sup>a</sup>        | 4  |
| 3     | 5 hrs       | 60         | 78 <sup>a</sup>        | 5  |
| 4     | 6 hrs       | 60         | 68 <sup>a</sup>        | 11   |
| 5     | No Reaction | 60         | -----                  | None (Only 30 μL of 10 <sup>-3</sup> M Pd <sup>2+</sup> ions solution) |

<sup>a</sup>under aerial conditions. <sup>b</sup>Isolated yields determined after recrystallization.



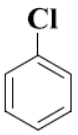
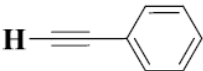
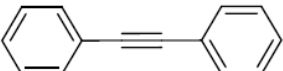
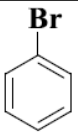
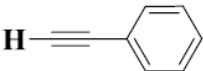
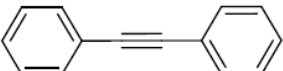
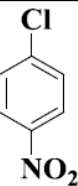
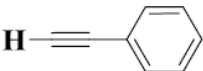
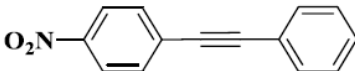
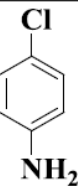
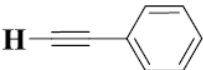
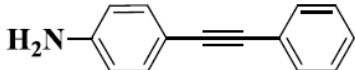
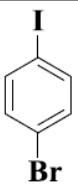
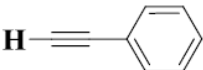
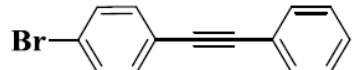
**11 (6 in manuscript)**

**Table S5:** Sonogashira coupling of different aryl halides and alkynes catalyzed by *in situ* generated Pd(0) nanoparticles.

| Entry | Halide   | Alkyne   | Product  | Solvent                            | Time   | Temp. (°C) | Yield <sup>b</sup> (%) |
|-------|--|--|--|------------------------------------|--------|------------|------------------------|
| 1     | <br><b>12</b>   | <br><b>9</b>    | <br><b>13</b>   | H <sub>2</sub> O/<br>EtOH<br>(7:3) | 5 h    | RT         | 90 <sup>a</sup>        |
| 2     | <br><b>14</b>   | <br><b>9</b>    | <br><b>15</b>   | H <sub>2</sub> O/<br>EtOH<br>(7:3) | 2.5 h  | RT         | 97 <sup>a</sup>        |
| 3     | <br><b>16</b>  | <br><b>17</b>  | <br><b>18</b>  | H <sub>2</sub> O/<br>EtOH<br>(7:3) | 50 min | 40         | 93                     |
| 4     | <br><b>19</b> | <br><b>17</b> | <br><b>20</b> | EtOH/<br>H <sub>2</sub> O<br>(3:7) | 50 min | 40         | 95                     |
| 5     | <br><b>21</b> | <br><b>17</b> | <br><b>22</b> | H <sub>2</sub> O/<br>EtOH<br>(7:3) | 50 min | 40         | 94                     |

<sup>a</sup>under aerial conditions. <sup>b</sup>Isolated yields determined after recrystallization.

**Table S6:** Sonogashira coupling of phenylacetylene with various aryl halides catalyzed by in situ generated Pd(0) nanoparticles.

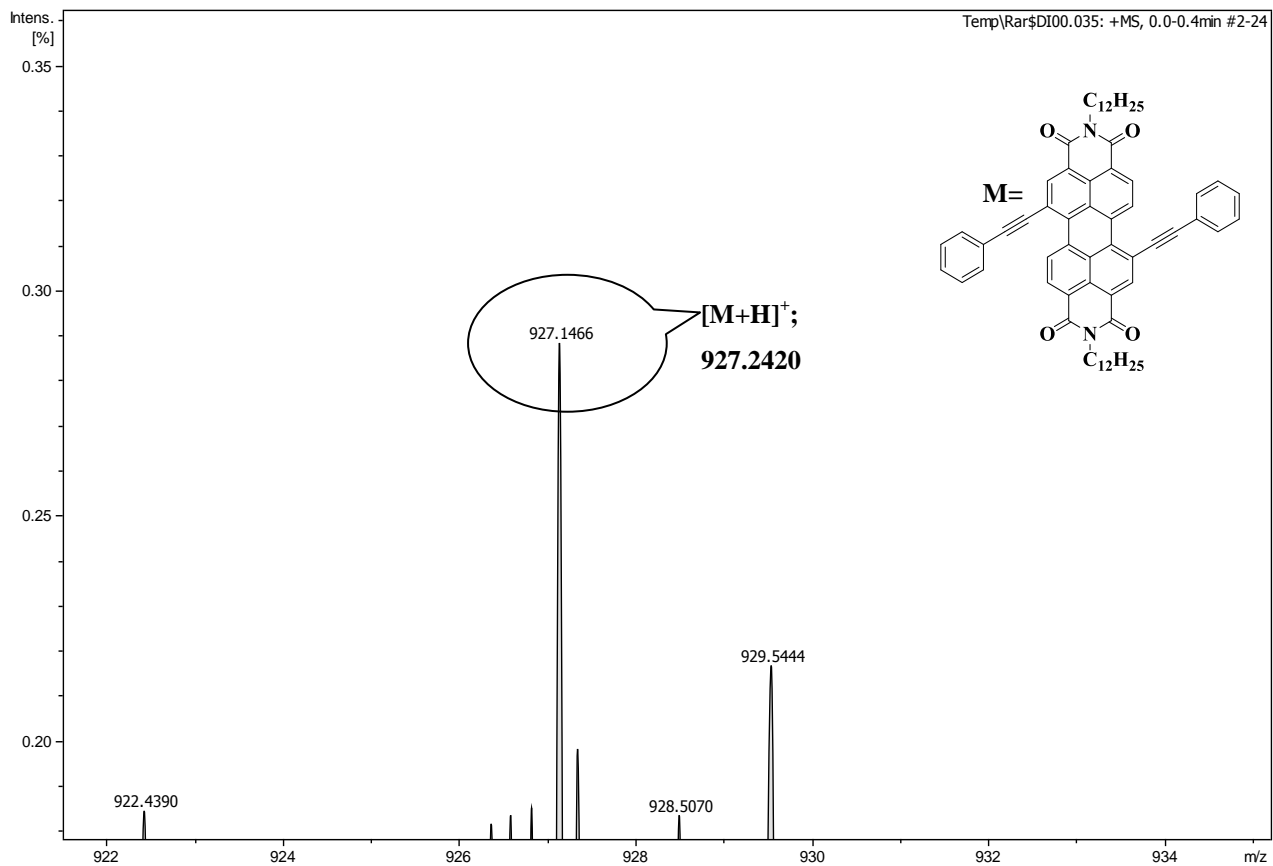
| Entry | Halide  | Alkyne   | Product  | Time   | Temp. (°C) | Yield <sup>b</sup> (%) |
|-------|---|--|--|--------|------------|------------------------|
| 1     | <br>23   | <br>9   | <br>10   | 55 min | 60         | 92                     |
| 2     | <br>24   | <br>9   | <br>10   | 50 min | 60         | 95                     |
| 3     | <br>25  | <br>9   | <br>15   | 7 h    | 90         | 94                     |
| 4     | <br>26 | <br>9 | <br>13 | 10 h   | 90         | 90                     |
| 5     | <br>27 | <br>9 | <br>28 | 50 min | RT         | 94 <sup>a</sup>        |

<sup>a</sup>under aerial conditions. <sup>b</sup>Isolated yields determined after recrystallization.

**Table S7:** Pd NPs catalyzed Sonogashira cross coupling reaction between iodobenzene and phenyl acetylene using various amounts of Pd NPs<sup>a</sup>.

| Entry | Pd NPs<br>( mole %) | Time (h) | Yield (%) | TON      | TOF (h <sup>-1</sup> ) |
|-------|---------------------|----------|-----------|----------|------------------------|
| 1     | 1                   | 0.2      | 96        | 9.6      | 48                     |
| 2     | 0.1                 | 0.3      | 96        | 96       | 320                    |
| 3     | 0.01                | 0.7      | 94        | 940      | 1342.85.               |
| 4     | 0.001               | 1.5      | 90        | 9000     | 6000                   |
| 5     | 0.0003              | 15       | 83        | 27666.66 | 1844.44                |
| 6     | 0                   | 15       | 0         | 0        | 0                      |

<sup>a</sup> All the reactions were carried out using 1 mmol of halide, 1 mmol of alkyne, 1 mmol of K<sub>2</sub>CO<sub>3</sub> in the presence of various amounts of Pd NPs in H<sub>2</sub>O/EtOH (7:3) solvent system at 60°C.



**Fig. S28** Mass Spectrum (ESI-MS) of compound **7**.