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Aggregates of pentacenequinone derivative as reactors for the preparation of Ag@Cu₂O core-shell NPs: An active photocatalyst for Suzuki and Suzuki type coupling reactions

Kamaldeep Sharma, Manoj Kumar and Vandana Bhalla* Department of Chemistry, UGC-Centre for Advanced Studies, Guru Nanak Dev University, Amritsar, Punjab, India. Email : vanmanan@yahoo.co.in

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General experimental Procedures:

Materials

All reagents were purchased from Aldrich and were used without further purification. THF was dried over sodium and benzophenone and kept over molecular sieves overnight before use. Silica gel (60–120 mesh) was used for column chromatography.

Instruments

UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length, 1 cm). The cell holder was thermostatted at 25 \degree C. The fluorescence spectra were recorded on a SHIMADZU 5301 PC spectrofluorimeter. Scanning electron microscope (SEM) images were obtained with a field-emission scanning electron microscope (SEM CARL ZEISS SUPRA 55). TEM images were recorded from Transmission Electron Microscope (TEM)-JEOL 2100F. Infrared spectrum was recorded on Varian 660-IR spectrometer. Photocatalytic experiments were carried out by using the 100 W tungsten filament bulb as irradiation source located inside the reactor. The ¹H NMR spectra were recorded on a JEOL-FT NMR-AL 300 MHz and Bruker-FT NMR-AL 500 MHz spectrophotometers using CDCl₃ as solvent and tetramethylsilane (SiMe₄) as internal standards. UV-vis studies were performed in THF and H₂O/THF mixture. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, br = broad, m = multiplet), coupling constants J (Hz), integration and interpretation.

Method of preparation of	Nanoparticles	Temp. (° C)	Time	Reducing agent	Special additive or	Shape of Core-shell	Recyclabi lity	Application of nanoparticles	Journals
nanoparticles					surfactant	NPs	/Reusabil ity		
Wet chemical method	Ag@Cu ₂ O	Room temp.	5 min.	No	No	Spherical	Yes	Photocatalytic Suzuki-Miyaura coupling	Present manuscript
Solution process	Au@Cu ₂ O	Room temp.	10 min	N_2H_4 · 3H ₂ O	Polyvinylpyrr olidone (PVP)	Spherical	No	Gas sensor applications	<i>Nanoscale</i> , 2014, 6 , 581–588
Solution process	Ag@Cu ₂ O	Room temp.	10 min	N ₂ H ₄	Polyvinylpyrr olidone (PVP)	Cubic	No	Evaluation of Optical properties	J. Phys. Chem. C 2014, 118 , 19948–19963
In-situ method	Ag@Cu ₂ O	80 °C	35 min.	-	Sodium citrate sodium carbonate	Nearly Spherical	No	Surface-enhanced (resonance) Raman scattering properties	<i>RSC Adv.</i> , 2014, 4 , 17249–17254
Solution process	Ag@Cu ₂ O	Room temp.	1 hr.	N_2H_4 · H_2O	-	Nanowires	No	Photocatalytic degradation of methyl orange	ACS Appl. Mater. Interfaces, 2014 , 6 , 15716–15725
Solution process	Au@Cu ₂ O	-	2 hrs.	NH ₂ OH·H Cl	Sodium dodecyl sulfate (SDS)	Spherical	No	Nanoreactors for gas sensor Applications	ACS Appl. Mater. Interfaces, 2014, 6 , 7491–7497
Chemical method	Ag@Cu ₂ O	-	2 hrs.	NH2OH· HCl	Sodium dodecyl sulfate (SDS)	Nearly Spherical	No	Photocatalytic degradation of methyl orange	ACS Catal. 2013, 3 , 47–51
Seed-based method	Ag@Cu ₂ O	120	24 hrs.	borane– tert- butylamin e complex	No	Nanoconcav es	Yes	Sonogashira-type oxidative arylation of phenylacetylene	Angew. Chem. 2013, 125 , 11255 -11259
Chemical method	(Pt, Pd, Ag, Au)– Cu ₂ O	Room temp.	2 hrs.	NH2OH· HCl	Sodium dodecyl sulfate (SDS)	cube	No	Reduction of 4- nitrophenol	J. Mater. Chem. A, 2013, 1 , 1763– 1769
Solution process	Au@Cu2O	-	-	NH4OH·H Cl	Sodium dodecyl sulfate (SDS)	NanoSphere	No	Degradation of methyl orange.	J. Am. Chem. Soc. 2012, 134 , 15033–15041
Solution process	Au@Cu ₂ O	-	2 hrs.	NH2OH. HCl	Sodium dodecyl sulfate (SDS)	Icosahedral	No	Effects of polyhedral gold nanocrystal morphology and facets on the formation of Au-Cu ₂ O Heterostructures	Chem. Mater. 2011, 23 , 2677– 2684
Photochemical method	Ag/Cu ₂ O and Au/Cu ₂ O	Room temp.	12 min	$\begin{array}{c} N_2H_4 \cdot \\ H_2O \end{array}$	Polyvinylpyrr olidone (PVP)	Spherical	No	Evaluation of Geometrically Tunable Optical Properties	Chem. Mater. 2011, 23, 4587– 459
Solution process	Au@Cu2O	-	2 hrs.	NH2OH· HCl	Sodium dodecyl sulfate (SDS)	Octahedral	No	Heterostructures with Precise Morphological Control	J. Am. Chem. Soc. 2009, <i>131</i> , 17871– 17878

Table S1: Comparison of this method in present manuscript for the preparation of $Ag@Cu_2O$ core-shell NPs over other reported procedures in literature for the preparation of Cu_2O based core-shell nanoparticles.

Table S2: Comparison of catalytic activity $Ag@Cu_2O$ for the photocatalytic Suzuki-coupling reactions over other photocatalysts reported in literature.

Entry	Source of light	Photo catalyst	Reaction conditions	Reaction temp.	Time	Recycla bility	Journals
1	100 W tungsten filament bulb	Ag@Cu ₂ O	H ₂ O/EtOH (3:1), K ₂ CO ₃ (1.5 eq.)	Room temp.	5 hr	Yes	Present manuscript
2	White LED lamp	Pd@B-BO3	DMF/H ₂ O (1:1), K ₂ CO ₃ (1.5 eq.)	Room temp.	2 hr	Yes	<i>Chem. mater.</i> 2015, 27 , 1921
3	300 W Xe lamp	Pd/SiC	DMF/H ₂ O (3:1), Cs ₂ CO ₃ (3 eq.)	30 °C	1.33 hr	Yes	J. Phys. Chem. C 2015, 119 , 3238–3243
4	Halogen lamp	Au–Pd alloy NP	DMF/H ₂ O (3:1), K_2CO_3 (3 eq.), Ar atmosphere	30 °C	6 hr	No	<i>Green Chem.</i> , 2014, 16 , 4272– 4285
5	500 W Xe lamp	Ru–Pd bimetallic complex	EtOH, PPh ₃ , K ₂ CO ₃ , Ar- atmosphere	Room temp.	6 hr	No	<i>Chem. Commun.</i> , 2014, 50 , 14501-14503
6	300 W Xe lamp with UV cutoff filter	GO–Pd@Ag– AgBr	EtOH/H ₂ O (1:1), K ₂ CO ₃ (3 eq.)	Room temp.	2 hr	Yes	<i>RSC Adv.</i> , 2014, 4 , 39242–39247
7	Sunlight	Au–Pd nanostructures	NaOH, CTAB, H ₂ O	Room temp.	2 hr	Yes	J. Am. Chem. Soc. 2013, 135 , 5588–5601

Table S3. Ag@ Cu_2O NPs catalyzed photocatalytic Suzuki coupling reactions between various aryl halides and phenyl boronic acid.

	$X + A = K_2CC$ $R_1 + HO^B OH$ $1 (a-d) 2$	R ₁		
Entry	Reactant	Product	Time (hr)	Yield %
1	1a ; X = Cl, R ₁ = H	3a ; R₁= H	5	43 %
2	1b ; X = Br, R ₁ = H	3b ; R ₁ = H	5	75%
3	1c ; X = I, R ₁ = H	3c ; R ₁ = H	5	84%
4	1d ; X = I, R ₁ = Br	3d ; R ₁ = Br	5	81 %

Table S4. Scope of the photocatalytic Suzuki coupling reaction of bromobenzene with various boronic acids or pinacol esters using $Ag@Cu_2O$ NPs.

Ent ry	Catalyst used	Boronic acid/ester	Amount of catalyst	Reaction conditions	Time (hr)	Product	Yield %
1	Ag@Cu₂O	S ОН В ОН	0.02 mmol	H ₂ O/EtOH (3:1) Visible light	5	\$	82
2	Ag@Cu₂O		0.02 mmol	H₂O/EtOH (3:1) Visible light	5	NH ₂	78
3	Ag@Cu₂O	но в-Сно но	0.02 mmol	H₂O/EtOH (3:1) Visible light	5	()-()-сно	70

Table S5. Scope of the photocatalytic Suzuki coupling reaction of various aryl bromides with phenyl boronic acid using Ag@Cu₂O NPs.

$\begin{array}{c} \begin{array}{c} R_{1} \\ R_{2} \\ R_{1} \\ R_{2} \\ R_{2} \\ R_{2} \\ R_{2} \\ R_{2} \\ R_{1} \\ R_{1} \\ R_{2} \\ R_{2} \\ R_{1} \\ R_{2} \\ R_$						
Entry	Reactant	Product	Time (hr)	Yield ∞∕		
				/0		
1	4a ; R ₁ =H, R ₂ =H	3a = 5a ; R ₁ =H, R ₂ =H	5	75		
2	4b ; R ₁ =OCH ₃ , R ₂ = OCH ₃	5b ; R ₁ =OCH ₃ , R ₂ = OCH ₃	5	82		
3	4c ; R ₁ = CH ₃ , R ₂ =H	5c ; R ₁ = CH ₃ , R ₂ =H	5	79		
4	4d ; R ₁ =CHO, R ₂ =H	5d ; R ₁ =CHO, R ₂ =H	5	71		
5	4e ; R ₁ =COOH, R ₂ =H	5e ; R ₁ =COOH, R ₂ =H	5	70		

Table S6. Mechanistic study of the photocatalytic Suzuki coupling reaction using Ag@Cu₂O NPs photocatalyst.

Entry	Catalyst used	Amt. of catalyst	Reaction conditions	Base	Time (hr)	Yield %
1	Ag@Cu₂O+TEOA	0.02 mmol	H ₂ O/EtOH (3:1) Visible light	K ₂ CO ₃ (1.5 eq.)	5	30
2	Ag@Cu ₂ O + Benzoquinone	0.02 mmol	H ₂ O/EtOH (3:1) Visible light	K₂CO₃ (1.5 eq.)	5	35
3	Ag@Cu₂O+TEOA+ Benzoquinone	0.02 mmol	H ₂ O/EtOH (3:1) Visible light	K ₂ CO ₃ (1.5 eq.)	5	~10

Synthesis of silver nanoparticles:

The spherical silver nanoparticles (AgNPs) were synthesized by reducing the AgNO₃ with aggregates of derivative **1** according to the previously reported procedure.¹ In detail, synthesis of AgNPs was carried out at room temperature which involves the preparation of mixed aqueous solutions of derivatives **1** (H₂O/THF 9.5/0.5), containing aqueous solution of AgNO₃. In a typical procedure, the reaction solutions were prepared by mixing 0.1 M AgNO₃ (30 μ L) with mixed aqueous solution of derivative **1**, (3 mL, 10 μ M) to obtain a homogeneous reaction mixture. The reaction mixture was stirred at room temperature, yielding the grey yellow Ag NPs. These AgNPs were washed 3-4 times with distilled water to remove unreacted AgNO₃ and used as such for further application.

Preparation of Benedict's stock solution

First dissolve 100 g sodium carbonate and 173 g sodium citrate dihydrate in a final volume of 850 mL water. Slowly, with stirring, add a solution of 17.3 g copper sulfate pentahydrate in 100 mL of water. Bring the final volume to one liter.

Synthesis of Ag@Cu₂O core-shell NPs:

Synthesis of Ag@Cu₂O core-shell NPs was carried out by a simple solution process which involved the synthesis of Cu₂O NPs by aggregates of derivative **1** and their subsequent deposition on spherical AgNPs. In a typical procedure, same amount of Benedict's solution (0.04 M) and washed AgNPs solution were mixed at room temperature. Then, solution of aggregates of derivative **1** (1 mM) in H₂O/THF (9.5:0.5) mixture was added slowly to the mixture with vigorous stirring. Immediately the solution color was changed from dark blue to dark green indicating the formation of Ag@Cu₂O core-shell NPs. After continuous stirring the mixture for 5-10 min. at room temperature, black coloured precipitates were observed. The resulting solution was sonicated to get homogeneous mixture before using in photocatalytic experiments.

¹ K. Sharma, G. Singh, G. Singh, M. Kumar and V. Bhalla, *RSC Adv.*, 2015, 5, 25781–25788.

General experimental procedure for photocatalytic Suzuki-Miyaura coupling reaction:

To a 25 ml Round Bottom Flask (RBF) were added bromobenzene (0.192 mmol, 30 mg), phenyl boronic acid (0.192 mmol, 29.67 mg), K_2CO_3 (0.288 mmol, 39.74 mg) and 0.02 mmol Ag@Cu₂O NPs in H₂O/EtOH (3:1) mixture. The reaction mixture was degassed with vacuum pump for 2-3 min. and then irradiated at a distance of 10 cm with a 100 W tungsten filament bulb (0.4 W/cm²) to provide visible light for 5 h under magnetic stirrer. The temperature of the reactant solution was maintained at room temperature by a water bath during the reaction. After completion of the reaction, solvent was evaporated under vacuum and extracted with dichloromethane. The pure product was then isolated by extracting the reaction mixture with hexane.

General experimental procedure for photocatalytic Suzuki type cross-coupling reaction:

To a 25 ml Round Bottom Flask (RBF), were added *N*-tosyl-aziridine (0.254 mmol, 50 mg), phenylboronic acid (0.279 mmol, 43.03 mg), K_2CO_3 (0.381 mmol, 52.58 mg) and 0.04 mmol Ag@Cu₂O NPs in H₂O/EtOH (3:1) mixture. The RBF was capped with a septum rubber, degassed with vacuum pump for 2-3 min. and then irradiated at a distance of 10 cm with a 100 W tungsten filament bulb (0.4 W/cm²) to provide visible light for 5 h under magnetic stirrer. The temperature of the reactant solution was maintained at 25 °C by a water bath during the reaction. After completion of the reaction, solvent was evaporated under vacuum and extracted with dichloromethane. The pure product was then isolated by extracting the reaction mixture with hexane.



Fig. S1 (A) Fluorescence spectra showing the variation of fluorescence intensity of derivative 1 (10 μ M) in H₂O/THF mixture with different fractions of H₂O. $\lambda_{ex} = 315$ nm (B) UV-vis spectra showing the variation of absorbance of derivative 1 (10 μ M) in H₂O/THF mixture with different fractions of H₂O. Inset: enlarge UV-vis spectra of derivative 1 (10 μ M) with the addition of H₂O/THF mixture in the range of 425-600 nm showing level-off tail.



Fig. S2 SEM image of derivative 1 in H_2O/THF (9.5/0.5) mixture showing flake like morphology; scale bar 2 μ m.



Fig. S3 Schematic diagram for the formation of Cu_2O and $Ag@Cu_2O$ core-shell NPs from benedict's solution on addition of pentacenequinone derivative 1.



Fig. S4 (A) UV-vis spectra of aqueous solution of Ag@Cu₂O core-shell NPs, AgNPs and Benedict's solution in the presence of AgNPs. UV-vis band at 470 nm and blue shifted band at 720 nm correspond to Ag core and Cu₂O shell. (B) UV-vis spectra with time for gradual addition of pentacenequinone aldehyde **1** (10 μ M) 100 μ L to the aqueous solution of Benedict's reagent and AgNPs.



Fig. S5 Graphical representation of rate of formation of $Ag@Cu_2O$ core-shell NPs generated by aggregates of pentacenequinone derivative **1**. (A) Time (min.) vs. absorbance plot at 470 nm (B) regression plot of A.

The first order² rate constant for the formation of $Ag@Cu_2O$ NPs was calculated from the change of intensity of absorbance of Benedict's reagent and AgNPs in the presence of aggregates of pentacenequinone derivative **1** at different time interval³.

From the time vs. absorbance plot at fixed wavelength 470 nm by using first order rate equation we get the rate constant = $k = slope \times 2.303 = 3.61 \times 10^{-4} s^{-1}$.

² Luty-Błocho, M.; Pacławski, K.; Wojnicki, M.; Fitzner, K. Inorganica Chimica Acta, 2013, 395 189–196.

³ (a) Sau, T. K.; Murphy, C. J. *Langmuir* **2004**, *20*, 6414. (b) Goswami, S.; Das, S.; Aich, K.; Sarkar, D.; Mondal, T. K.; Quah, C. K.; Fun, H-K. *Dalton Trans.* **2013**, *42*, 15113–15119.



Fig. S6 Fourier transforms infrared (FTIR) absorption spectrum of Ag@Cu₂O core-shell NPs.



Fig. S7 (A) SEM and (B) HRTEM images of generated Ag@Cu₂O core-shell NPs. Scale bar (A) 1µm and (B) 20 nm.



Average shell thickness = 9.7 nm

Average shell thickness = 10.2 nm

Average shell thickness = 11.0 nm

Fig. S8 Calculated average shell thickness of Cu_2O at different AgNPs to Benedict's solution ratio. Scale bar (A), (B) 20 nm and (C) 10 nm.



Fig. S9 Absorption spectra of $Ag-Cu_2O$ core-shell NPs showing red shifting of absorption band at 720 nm corresponding to Cu_2O with changing AgNPs to Benedict's solution ratio.



Fig. S10 X-Ray Diffraction (XRD) pattern of Ag@Cu₂O core-shell NPs.



Fig. S11 TEM image showing spherical shape of Cu₂O NPs. Scale bar 50 nm.



Fig. S12 X-Ray Diffraction (XRD) pattern of spherical Cu₂O NPs.



Fig. S13 The proposed mechanism for the photocatalytic Suzuki-Miyaura coupling reaction on Ag@Cu₂O core-shell NPs.



Fig. S14 TEM image of $Ag@Cu_2O$ NPs catalyst recovered after photocatalytic Suzuki coupling reaction. Scale bar 20 nm.

¹H NMR spectra of products of the photocatalytic Suzuki coupling reactions using different substrates.

Biphenyl (**3a**). ¹H NMR (300 MHz, CDCl₃): δ = 7.60 [d, 4H, J = 6.9 Hz, ArH], 7.44 [t, 4H, J = 7.4 Hz, ArH], 7.36 [d, 2H, J = 7.5 Hz, ArH]



Fig. S15 The ¹H NMR spectrum of biphenyl in CDCl₃.



4-bromo-1,1'-biphenyl (3d). ¹H NMR (500 MHz, CDCl₃): δ = 7.35 [d, 2H, J = 8.5 Hz, ArH], 7.33 [d, 2H, J = 8.5 Hz, ArH], 7.11 [t, 2H, J = 9.2 ArH], 7.04-7.00 [m, 3H, ArH]

Fig. S16 The ¹H NMR spectrum of 4-bromo-1,1'-biphenyl in CDCl₃.



3-Phenyl-thiophene: ¹H NMR (500 MHz, CDCl₃) δ 7.53 [d, 2H, J = 8.5 Hz, ArH], 7.48-7.46 [m, 1H], 7.39-7.34 [m, 4H, ArH], 7.30-7.29 [m, 1H, ArH].

Fig. S17 The ¹H NMR spectrum of 3-Phenyl-thiophene in CDCl₃.

4-Aminobiphenyl: ¹H NMR (500 MHz, CDCl₃) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 8.5 Hz, 4H), 6.81 (t, *J* = 7.5 Hz, 1H), 6.53 (d, *J* = 8.5 Hz, 2H), 3.70 (s, 2H).



Fig. S18 The ¹H NMR spectrum of 4-Amino-biphenyl in CDCl₃.

4-Formylbiphenyl: ¹H NMR (500 MHz, CDCl₃) δ 9.95 (s, 1H), 7.81 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 7.5 Hz, 2H), 7.28-7.31 (m, 3H).



Fig. S19 The ¹H NMR spectrum of 4-formyl-biphenyl in CDCl₃.

3,4-dimethoxybiphenyl (5b): ¹H NMR (500 MHz, CDCl₃): δ 7.58 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 7.5 Hz, 1H), 7.44 (d, J = 7.5 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.17 (dd, J = 7.5, 1.5 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 6.97 (d, J = 8.5 Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H), ppm.



Fig. S20 The ¹H NMR spectrum of 3,4-dimethoxybiphenyl in CDCl₃.



4-methyl-1,1'-biphenyl (5c): ¹H NMR (500 MHz, CDCl₃) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.53-7.48 (m, 3H), 7.42 (d, J = 8.5 Hz, 2H), 2.05 (s, 3H).

Fig. S21 The ¹H NMR spectrum of 4-methyl-1,1'-biphenyl in CDCl₃.



[1,1'-biphenyl]-4-carboxylic acid (5e): ¹H NMR (500 MHz, CDCl₃): δ 7.85 (d, J = 6.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.41–7.35 (m, 3H)

Fig. S22 The ¹H NMR spectrum of [1,1'-biphenyl]-4-carboxylic acid in CDCl₃.

¹H NMR spectra of products of the photocatalytic Suzuki type coupling reactions using different substrates.

4-methyl-N-phenethylbenzenesulfonamide (**10**): ¹H NMR (300 MHz, CDCl₃) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.70-7.63 (m, 5H), 7.32 (d, *J* = 6.6 Hz, 2H), 4.97 (br s, 1H), 3.35 (t, *J* = 7.8 Hz, 2H), 3.19 (t, J = 5.4 Hz, 2H), 2.41 (s, 3H)



Fig. S23 The ¹H NMR spectrum of 4-methyl-N-phenethylbenzenesulfonamide in CDCl₃.

4-methyl-N-(2-(thiophen-3-yl)ethyl)benzenesulfonamide (11): ¹H NMR (300 MHz, CDCl₃) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.35 (s, 1H), 7.29 (d, *J* = 6.6 Hz, 2H), 7.11 (d, *J* = 6.3 Hz, 1H), 6.96 (d, *J* = 6.6 Hz, 1H), 4.70 (br s,1H), 3.60 (t, *J* = 4.95 Hz, 2H), 3.01 (t, J = 5.1 Hz, 2H), 2.41 (s, 3H)



Fig. S24 The ¹H NMR spectrum of 4-methyl-N-(2-(thiophen-3-yl)ethyl)benzenesulfonamide in CDCl₃.

N-(4-formylphenethyl)-4-methylbenzenesulfonamide (12): ¹H NMR (300 MHz, CDCl₃) δ 9.97 (s, 1H), 7.86 (d, J = 8.7 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 6.6 Hz, 2H), 4.76 (br s, 1H), 3.64 (t, J = 5.1 Hz, 2H), 3.02 (t, J = 5.4 Hz, 2H), 2.41 (s, 3H)



Fig. S25 The ¹H NMR spectrum of N-(4-formylphenethyl)-4-methylbenzenesulfonamide in CDCl₃.

N-(4-aminophenethyl)-4-methylbenzenesulfonamide (**13**): ¹H NMR (300 MHz, CDCl₃) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.29 (2H, d, *J* = 6.6 Hz), 7.13 (2H, d, *J* = 7.5 Hz), 6.66 (d, *J* = 7.8 Hz, 2H), 4.76 (br s,1H), 3.60 (s, 2H), 2.99 (br t, 2H), 2.81 (t, J = 7.2, 2H), 2.41 (s, 3H)



Fig. S26 The ¹H NMR spectrum of N-(4-aminophenethyl)-4-methylbenzenesulfonamide in CDCl₃.

4-(6,13-dioxo-6,13-dihydropentacen-2-yl)benzaldehyde (8): ¹H NMR (300 MHz, CDCl₃) δ 10.03 (s, 1H, CHO), 9.07-8.99 (m, 4H, ArH), 8.23 (s, 1H, ArH), 8.18-8.11 (m, 3H, ArH), 7.83 (d, *J* = 7.8 Hz, 1H, ArH), 7.80-7.73 (m, 4H, ArH), 7.42 (d, *J* = 8.1 Hz, 2H, ArH)



Fig. S27 The ¹H NMR spectrum of 4-(6,13-dioxo-6,13-dihydropentacen-2-yl)benzaldehyde in CDCl₃.

4,4'-(6,13-dioxo-6,13-dihydropentacene-2,3-diyl)dibenzaldehyde (**1**): ¹H NMR (300 MHz, CDCl₃): δ = 10.05 [s, 2H, CHO], 9.06 [s, 2H, ArH], 9.00 [s, 2H, ArH], 8.25 [s, 2H, ArH], 8.21-8.15 [m, 2H, ArH], 7.85 [d, 4H, J = 9.6 ArH], 7.78-7.74 [m, 2H, ArH], 7.44 [d, 4H, J = 7.8 Hz, ArH],;



Fig. S28 The ¹H NMR spectrum of 4,4'-(6,13-dioxo-6,13-dihydropentacene-2,3-diyl)dibenzaldehyde in CDCl₃.