Self-assembly of a Pd^{II} neutral molecular rectangle *via* a new organometallic Pd^{II}_2 molecular clip and oxygen donor linker†

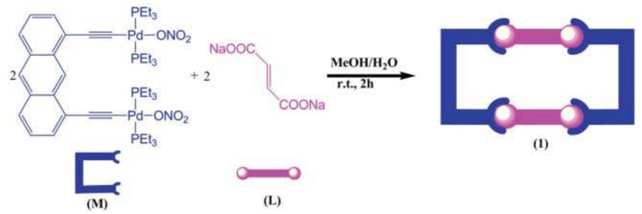
Arun Kumar Bar, Bappaditya Gole, Sushobhan Ghosh and Partha Sarathi Mukherjee*

Received 12th June 2009, Accepted 19th June 2009
First published as an Advance Article on the web 24th June 2009
DOI: 10.1039/b911622m

Two components self-assembly of a Pd_4 neutral molecular rectangle driven by Pd–O bond coordination has been achieved and this π-electron rich rectangle shows fluorescence quenching in presence of nitroaromatics, which are the chemical signatures of many explosives.

The coordination driven self-assembly of supramolecular entities of transition metals has received considerable attention during the past decade due to their potential for application as sensors, catalysts and in host–guest chemistry.[1] The important aspects of this methodology are the rational design of structures of diverse shapes and sizes as well as functionalization by incorporating suitable functional groups.[2] For design and synthesis of such assemblies of finite shapes and sizes, Pd^{II} and Pt^{II} have long been used as the acceptors of choice in view of their rigid square planar coordination environment.[1] Nitrogen donor symmetrical polypyridyl ligands have been used widely with these metal ions to prepare several 2D and 3D architectures with a few exceptions where Pt^{II} based neutral macrocycles have also been synthesized.[3] In a majority of the cases, finite assemblies of these metal ions are the derivatives of *cis*-blocked 90° metal acceptors. However, Stang and others have reported many shape selective Pt^{II}_2 or Pt^{II}_3 linkers and their self-assembly of various interesting architectures like hexagon, pentagon, dodecahedron *etc.*, which are not possible to obtain from *cis*-blocked acceptors.[2a–b,4] Interestingly, such an approach of designing interesting architectures using suitable shape-selective polypalladium linkers has not yet been explored.

Hence, the reported Pd^{II} architectures are generally restricted to the derivatives of *cis*-blocked Pd^{II} acceptors or of free $Pd(NO_3)_2$.[5] Here we report the synthesis and characterization of a novel Pd^{II}_2 shape selective organometallic molecular "clip" (M) and it's self-assembly of a neutral molecular rectangle (**1**) using linear dicarboxylate donor fumarate (L) (Scheme 1). Rectangle **1** represents a very rare example of a Pd^{II} neutral macrocycle obtained using Pd–O coordination bonding as driving force. While oxygen based hard donors are expected to be unsuitable for soft acid Pd^{II}, the electrostatic interaction between the anionic fumarate and Pd^{II} played an important role to obtain this unique Pd–O bond directed neutral rectangle.



Scheme 1 Formation of **1** by [2 + 2] self-assembly of the Pd^{II}_2-clip and fumarate linker.

Of the various geometries accessible through directional bonding approach, tetranuclear squares and dinuclear rhomboids have dominated the literature.[1] Despite their structural simplicity, molecular rectangles represent a unique class of macrocycle because their synthesis remains a challenge. The first idea that one can imagine for designing a rectangle is the [4 + 2 + 2] self-assembly of a *cis*-blocked 90° acceptor in combination with two linear donors of different lengths (ESI).† Only a very few examples are known in the literature where rhenium based rectangles have been prepared using this approach.[6] However, no handful example of rectangle is known for Pt^{II} or Pd^{II} metals using this approach. The main disadvantage of this three-components assembly is the non-selectivity in formation of the desired rectangle because of the possibility of formation of a mixture of squares of different sizes from the combination of 90° corners with individual linear linkers. Our strategy for the synthesis of molecular rectangle utilizes [2 + 2] self-assembly of a molecular "clip" (M) with a linear donor fumarate (L).

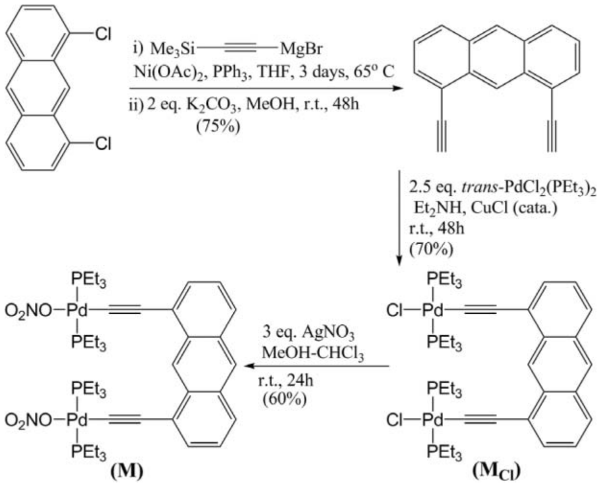
Synthesis of M is successfully performed in three steps from 1,8-dichloroanthracene. 1,8-diethynylanthracene was obtained by treating 1,8-dichloroanthracene with (trimethylsilyl)acetylide magnesium bromide ($Me_3SiCCMgBr$) under an inert atmosphere followed by hydrolysis with K_2CO_3 in methanol medium. Reaction of 1,8-diethynylanthracene with 2.5 equivalents of *trans*-$Pd(PEt_3)_2Cl_2$ in the presence of CuCl catalyst in dry diethylamine yielded the dichloro derivative (M_{Cl}) of the "clip" M. M was prepared by treating the dichloro derivative with three equivalents of $AgNO_3$ (Scheme 2).

The dichloro "clip" M_{Cl} is yellow crystalline, soluble in THF, dichloromethane and chloroform. ^1H NMR spectrum showed the expected peaks (Fig. 1) with appropriate integration ratios, and ^{31}P NMR spectra showed single peak at 17.79 ppm. Finally, the molecular structure of M_{Cl} was unambiguously established by an X-ray single crystal diffraction method.‡ Suitable single crystals for X-ray diffraction were obtained by slow evaporation of the chloroform solution of M_{Cl}. Fig. 2 represents the view of the molecular structure of the clip M_{Cl}. The coordination geometry around each Pd^{II} is square planar with P_2CCl environment. The

---

Inorganic and Physical Chemistry Department, Indian Institute of Science, Bangalore-560012, India. E-mail: psm@ipc.iisc.ernet.in; Fax: +91-80-2360-1552; Tel: +91-80-2293-3352

† Electronic supplementary information (ESI) available: Crystallographic information of M_{Cl} in CIF format, ^{13}C NMR of M, fluorescence quenching plot of **1** in presence of nitroaromatics. CCDC reference number 732627. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b911622m



Scheme 2 Synthesis of the molecular clip M.

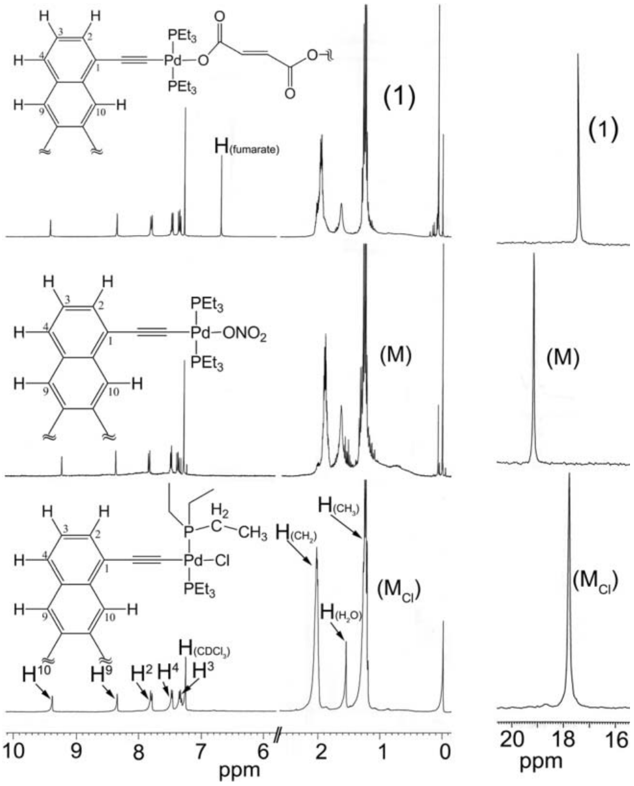


Fig. 1 ^1H (left) and $^{31}P\{^1H\}$ (right) NMR spectra of M_{Cl}, M and the rectangle **1**.

structure of this clip belongs to monoclinic crystal system with $C2/c$ space group. The asymmetric unit contains half of the clip and total clip structure is generated by C_2-symmetry through C9 and C10 (Fig. 2). Crystallographic refinement details including selected bond parameters are given in the ESI.† Intramolecular Pd–Pd distance was calculated to be 6.396 Å. Interestingly, the synthesis of such "clip" using *trans*-$Pd(PEt_3)_2I_2$ instead of *trans*-$Pd(PEt_3)_2Cl_2$ was unsuccessful. Moreover, substitution of Pd–Cl bonds in M_{Cl} by treating with iodide resulted in the formation of *trans*-$Pd(PEt_3)_2I_2$ by the cleavage of C(ethynyl)–Pd bonds. Coordination planes of both the palladium atoms are almost perpendicular to the plane of anthracene moiety. The palladium containing ethynyl arms of the molecular "clip" are not perfectly parallel rather they are slightly pushed outward due to steric hindrance among neighbouring PEt_3 groups.

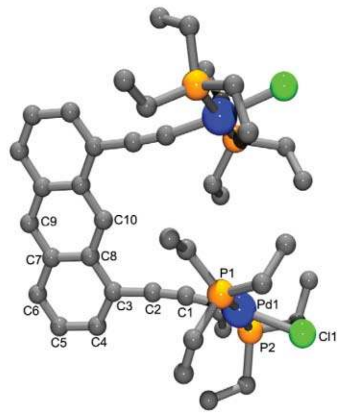


Fig. 2 Ball and stick view of the molecular structure of M_{Cl} with colour codes (grey = C; blue = Pd; green = Cl; yellow = P).

Formation of large supramolecules using Pd^{II}–O coordination as a driving force is expected to be unsuitable due to weak bonding interaction between a soft Pd^{II} acceptor and a hard oxygen donor. Our earlier effort using *cis*-(dppf)Pd(OTf)$_2$ as a 90° acceptor in combination with α,β-unsaturated fumarate dicarboxylate resulted unusual reduction of the C=C bond of fumarate followed by the formation of a metallochelate instead of an expected supramolecular macrocycle.[7]

When a methanolic solution of M was reacted with an aqueous solution of equimolar amount of Na_2-fumarate, **1** was formed as a fluorescent yellow precipitate in a few minutes in almost quantitative yield.[8] ^{31}P NMR of the yellow precipitate in $CDCl_3$ indicated the formation of a single and symmetrical product by the appearance of a single peak at δ 17.31 ppm, shifted 1.85 ppm upfield relative to M. ^1H NMR spectrum of the product also revealed the formation of a single and symmetrical product by the appearance of all expected peaks and displayed spectroscopic differences from starting linkers (Fig. 1).

Finally, formation of a [2 + 2] self-assembled product **1** was confirmed by MALDI-MS data which showed the presence of peaks at m/z = 2045.5 and 1957.9 corresponding to $[M_1 + H^+]$ and $[M_1 - PEt_3 + MeOH]$, respectively, where M_1 represents the molar mass of intact rectangle **1**. Our attempts to crystallize the rectangle **1** have so far been unsuccessful. A rectangle is the only possible discrete architecture for a [2 + 2] combination of the clip and a linear linker. To get an overall view and gross connectivity of the linkers in macrocycle **1**, we have optimized the structure. Optimization of the molecular rectangle was done using density functional theory (DFT) calculation. B3LYP functional was used for the calculation employing two types of basis sets, 6–31G for lighter element (C, H, O) and LanL2DZ for heavier element (Pd, P). A view of the optimized structure of the neutral macrocycle **1** is shown in Fig. 3.

Ethynyl functionality was introduced to make the final metallocycle π electron rich and fluorescent in nature having in mind that Pd–ethynyl compounds may show fluorescence behaviour. Discovery of fluorescent sensors for the selective detection of chemicals/ions has been a very active field of current research.

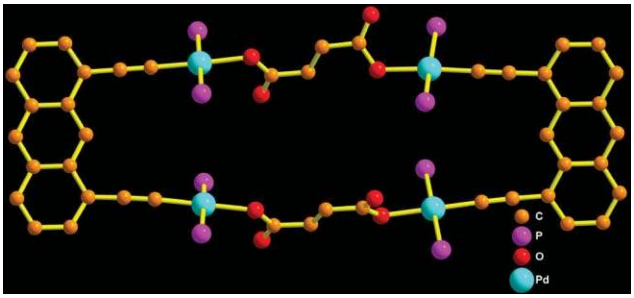


Fig. 3 View of the optimized structure of **1**. Ethyl groups have been removed for the sake of clarity.

Recently we have developed a Pt–ethynyl based fluorescent sensor for the detection of nitroaromatics, which are the chemical signatures of many explosives.[2a] On excitation at 400 nm, macrocycle **1** showed strong emission band at 440 nm in $CHCl_3$ medium. The fluorescence intensity at 440 nm was quenched efficiently upon gradual addition of TNT of the concentration of order 10^{-5} (M). Analysis of the normalized fluorescence intensity (I_0/I) as a function of quencher concentration [Q] was carried out by the Stern–Volmer equation $I_0/I = 1 + K_{SV}[Q]$. The Stern–Volmer constant (K_{SV}) in this case was calculated to be 1.32×10^4 M^{-1}.

In conclusion, we herein report the synthesis and characterization of a neutral Pd^{II}_4 molecular rectangle (**1**) prepared *via* directional self-assembly of a new organometallic Pd_2 molecular "clip" and fumarate anion. Complex **1** represents a very rare example of a neutral Pd^{II} supramolecular architecture prepared using Pd–O coordination as a driving force. Initial investigation suggests the fluorescent nature of **1** and the solution fluorescence intensity was quenched upon addition of electron deficient nitroaromatics. While Stang and others have reported many shape selective Pt^{II}_2 and Pt^{II}_3 linkers and their interesting architectures which are not possible to derive from widely available *cis*-blocked 90° acceptors or free metal ions, so far this approach is mainly restricted to Pt^{II}. Interestingly, reported Pd^{II} architectures are the derivatives of either *cis*-blocked Pd^{II} acceptors or of free $Pd(NO_3)_2$. Our present approach is a unique way using Pd^{II} shape selective linker to design molecular architecture which are not possible to synthesize from *cis*-blocked Pd^{II} acceptors or from free $Pd(NO_3)_2$. This approach may open up a new way of designing many unknown 2D and 3D Pd^{II} architectures using suitable Pd^{II}_2 and Pd^{II}_3 shape selective linkers, including functionalization by incorporating suitable receptors for the detection of selective analyte by fluorescence quenching method. Studies are under way to establish the full scope of this methodology.

Acknowledgements

We are grateful to the Department of Science and Technology, New Delhi, India for financial support to P. S. M. The authors sincerely thank the Johnson Matthey Public Ltd. U. K. for a generous supply of $PdCl_2$.

Notes and references

‡ Crystallographic data were collected at 293(2) K using Bruker X8 Apex II diffractometer equipped with monochromated Mo Kα radiation (λ = 0.71073 Å). Crystal data for molecular clip M_{Cl}: $C_{42}H_{68}Cl_2P_4Pd_2$, M_r = 980.54, monoclinic; space group $C2/c$; a = 26.723(3) Å; b = 12.9521(16) Å; c = 14.0694(18) Å; β = 100.178°(3); V = 4793.0(10) Å^3; Z = 4; reflections collected = 18 892; unique reflections = 4916; R_{int} = 0.0485; R_1 = 0.0572 (observed); R_1 = 0.1155 (total) and wR_2 = 0.1179.

1 (*a*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (*b*) E. Zangrando, M. Casanova and E. Alessio, *Chem. Rev.*, 2008, **108**, 4979; (*c*) G. F. Swiegers and T. J. Malefetse, *Coord. Chem. Rev.*, 2002, **225**, 91; (*d*) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; (*e*) B. H. Northrop, H.-B. Yang and P. J. Stang, *Chem. Commun.*, 2008, 5896; (*f*) B. Olenyuk and P. J. Stang, *Acc. Chem. Res.*, 1997, **30**, 502; (*g*) F. A. Cotton, C. Lin and C. A. Murillo, *Acc. Chem. Res.*, 2001, **34**, 759; (*h*) S.-S. Li, B. H. Northrop, Q.-H. Yuan, L.-J. Wan and P. J. Stang, *Acc. Chem. Res.*, 2009, **42**, 249; (*i*) J. Mattson, P. Govindaswamy, J. Furrer, S. Sei, K. Yamaguchi, G. Suss-Fink and B. Therrien, *Organometallics*, 2008, **27**, 4346; (*j*) N. L. Toh, N. Nagarithinum and J. J. Vittal, *Angew. Chem., Int. Ed.*, 2005, **44**, 2237.

2 (*a*) S. Ghosh and P. S. Mukherjee, *Organometallics*, 2008, **27**, 316; (*b*) S. Ghosh and P. S. Mukherjee, *Inorg. Chem.*, 2009, **48**, 549; (*c*) A. K. Bar, R. Chakrabarty, G. Mostafa and P. S. Mukherjee, *Angew Chem., Int. Ed.*, 2008, **47**, 8455; (*d*) S. Ghosh and P. S. Mukherjee, *J. Org. Chem.*, 2006, **71**, 8412; (*e*) P. S. Mukherjee, K. S. Min, A. M. Arif and P. S. Stang, *Inorg. Chem.*, 2004, **43**, 6345; (*f*) B. P. Dash, R. Satapathy, J. A. Maguire and N. S. Hosmane, *Org. Lett.*, 2008, **10**, 2247.

3 (*a*) N. Das, P. J. Stang and A. M. Arif, *J. Org. Chem.*, 2005, **70**, 10440; (*b*) P. S. Mukherjee, N. Das, Y. Kryschenko, A. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2004, **126**, 2464.

4 (*a*) M. Schweiger, R. S. Seidel, M. Schmitz and P. J. Stang, *Org. Lett.*, 2000, **2**, 1255; (*b*) B. Olenyuk, J. A. Whiteford, A. Fechtenkötter and P. J. Stang, *Nature*, 1999, **398**, 796; (*c*) C. J. Kuehl, S. D. Huang and P. J. Stang, *J. Am. Chem. Soc.*, 2001, **123**, 9634; (*d*) D. Kim, J. H. Paek, M.-J. Jun, J. Y. Lee and S. O. Kangand Ko, *J. Inorg. Chem.*, 2005, **44**, 7886; (*e*) M. R. J. Elsegood, M. B. Smith and P. M. Staniland, *Inorg. Chem.*, 2006, **45**, 6761.

5 (*a*) C. H. M. Amijs, G. P. M. van Klink and G. van Koten, *Dalton Trans.*, 2006, 308; (*b*) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawaand and K. Biradha, *Chem. Commun.*, 2001, 509; (*c*) A. Rang, M. Engeser, N. M. Maier, M. Nieger, W. Lindner and C. A. Schalley, *Chem.–Eur. J.*, 2008, **14**, 3855; (*d*) M. Fujita, M. Tominaga, A. Hori and B. B. Therrien, *Acc. Chem. Res.*, 2005, **38**, 369, and references therein.

6 P. Thanksekaran, R. T. Liao, Y. H. Liu, T. Rajendran, R. Rajagopal and K. L. Lu, *Coord. Chem. Rev.*, 2005, **249**, 1085, and references therein.

7 A. K. Bar, R. Chakrabarty and P. S. Mukherjee, *Organometallics*, 2008, **27**, 3806.

8 **Synthesis of 1,8-bis[*trans*-(ethynyl)Pd(PEt_3)$_3$Cl]anthracene (M_{Cl}):** To a 100 mL round bottom Schlenk flask, 1,8-diethynylanthracene (400.5 mg, 1.77 mmol) and *trans*-$Pd(PEt_3)_2Cl_2$ (1817.3 mg, 4.39 mmol) were added under N_2 atmosphere. 75 mL of dried and degassed Et_2NH was syringed into the flask. After 10 min stirring, CuCl (40 mg, ~6.6 mol%) was added. Immediately greenish yellow gelatinous fluorescent precipitate appeared and on stirring it assumed deep yellow reaction mixture. After 48 h stirring, the solvent was removed under vacuum yielding a brown solid. The crude solid was column chromatographed through silica gel (60–120 mesh) with first toluene–*n*-hexane (80 : 20 v/v) and then with ethylacetate. The fraction eluted with ethylacetate was concentrated to minimum volume and added *n*-hexane. On triturating yielded deep yellow powder as pure M_{Cl} in 70% isolated yield. Anal. calcd for $C_{42}H_{68}Pd_2Cl_2P_4$: C 51.44, H 6.99. Found: C 51.51, H 7.08. ^1H NMR (400 MHz; $CDCl_3$): δ/ppm = 9.39 (s, 1 H), 8.36 (s, 1 H), 7.8 (d, 2 H), 7.48 (d, 2 H), 7.36–7.32 (m, 2 H), 2.07–2.00 (m, 24 H), 1.33–1.15 (m, 36 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz) δ/ppm: 17.79 (s).$^{13}C\{^1H\}$($CDCl_3$) 132.44 (C_{10}, anthracene), 131.72 (C_9, anthracene), 129.89 (C_1, anthracene), 127.47 (C_{11}, anthracene), 126.82 (C_{12}, anthracene), 126.19 (C_2, anthracene), 125.59 (C_4, anthracene), 125.03 (C_3, anthracene), 106.24 ($C_{2'}$, ethynyl), 102.71 ($C_{1'}$, ethynyl), 20.45 (CH_2, Et), 9.11 (CH_3, Et). IR (KBr): ν(C≡C) = 2101 cm^{-1}. UV-vis ($CHCl_3$) λ_{max}/nm (ε/$cm^{-1}M^{-1}$): 214 (16 434), 263 (16 512), 361 (6290), 385 (6774), 405 (8590), 428 (8330), 883 (1568), 906 (1448). **Synthesis of 1,8-bis[*trans*-(ethynyl)Pd(PEt_3)$_3$(NO_3)]anthracene (M):** To a stirred solution of M_{Cl} (525.3 mg, 0.54 mmol) in 30 mL of degassed $CHCl_3$ was added the degassed methanolic solution (15 mL) of silver nitrate (273.1 mg, 1.6 mmol) under nitrogen atmosphere. The reaction mixture was stirred under nitrogen atmosphere at r.t. for 24 h in absence of light and filtered through the Celite-545, washed with $CHCl_3$. The filtrate and washings

were concentrated ~3 mL and cold diethyl ether was added to precipitate out (M) as brown solid in a 60% isolated yield. ^{1}H NMR (400 MHz; $CDCl_3$): δ/ppm = 9.24 (s, 1 H), 8.37 (s, 1 H), 7.84 (d, 2 H), 7.48 (d, 2 H), 7.38–7.34 (m, 2 H), 1.95–1.85 (m, 24 H), 1.34–0.98 (m, 36 H). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.4 MHz): 19.17 (s). ESI-Ms: m/z = 970.32 $[M - NO_3]^+$. Synthesis of **1**: In a 4 mL glass vial equipped with magnetic stir bar was taken solid M (24.1 mg, 0.023 mmol) and added minimum amount of MeOH required to dissolve the solid. Equimolar amount of disodiumfumarate (3.7 mg, 0.023 mmol) dissolved in minimum amount of water was added to the above solution. Yellow precipitate was formed in a few minutes. After 2 h of stirring the yellow solid was collected by centrifugation, washed with methanol and dried under vacuum to get **1** as yellow powder with good to excellent yield. Microcrystalline **1** was obtained from slow evaporation of chloroform or dichloromethane solution. Anal. calcd for $C_{92}H_{140}O_8P_8Pd4$: C 53.97, H 6.89. Found: C 53.51, H 7.00. MALDI-MS: 2045.5 (13%) [**1** + H$^+$]; Q-TOF-ESI: 1691.66 (100%) [**1** + H$^+$ − 3PEt$_3$]; ^{1}H NMR (400 MHz; $CDCl_3$): δ/ppm = 9.47 (s, 1 H), 8.41 (s, 1 H), 7.86 (d, 2 H), 7.52 (d, 2 H), 7.42–7.40 (m, 2 H), 2.1–2.00 (m, 24 H), 1.37–1.23 (m, 36 H). ^{31}P{1H} NMR ($CDCl_3$, 121.4 MHz) δ/ppm: 17.31 (s). ^{13}C{1H}($CDCl_3$) δ/ppm: 172.63 (C_a, fumarate carboxylate), 139.81 (C_b, fmarate), 136.03 (C_{10}, anthracene), 132.45 (C_9, anthracene), 129.94 (C_1, anthracene), 127.50 (C_{11}, anthracene), 126.86 (C_{12}, anthracene), 126.15 (C_2, anthracene), 125.59 (C_4, anthracene), 125.03 (C_3, anthracene), 106.24 ($C_{2'}$, ethynyl), 102.71 ($C_{1'}$, ethynyl), 20.44 (CH_3–CH_2–), 9.09 (CH_3–CH_2–). IR (KBr): ν(C≡C) = 2103 cm^{-1}. UV-vis ($CHCl_3$) λ_{max}/nm (ε/cm^{-1}M^{-1}): 279 (22 250), 400 (5334), 424 (4518).