Supplementary material (ESI) for Journal of Materials Chemistry

Supplementary Information for

"Direct" Grafting of Linear Macromolecular 'Wedges' to the Edge of Pristine Graphite to Prepare Edge-Functionalized Graphene-Based Polymer Composites

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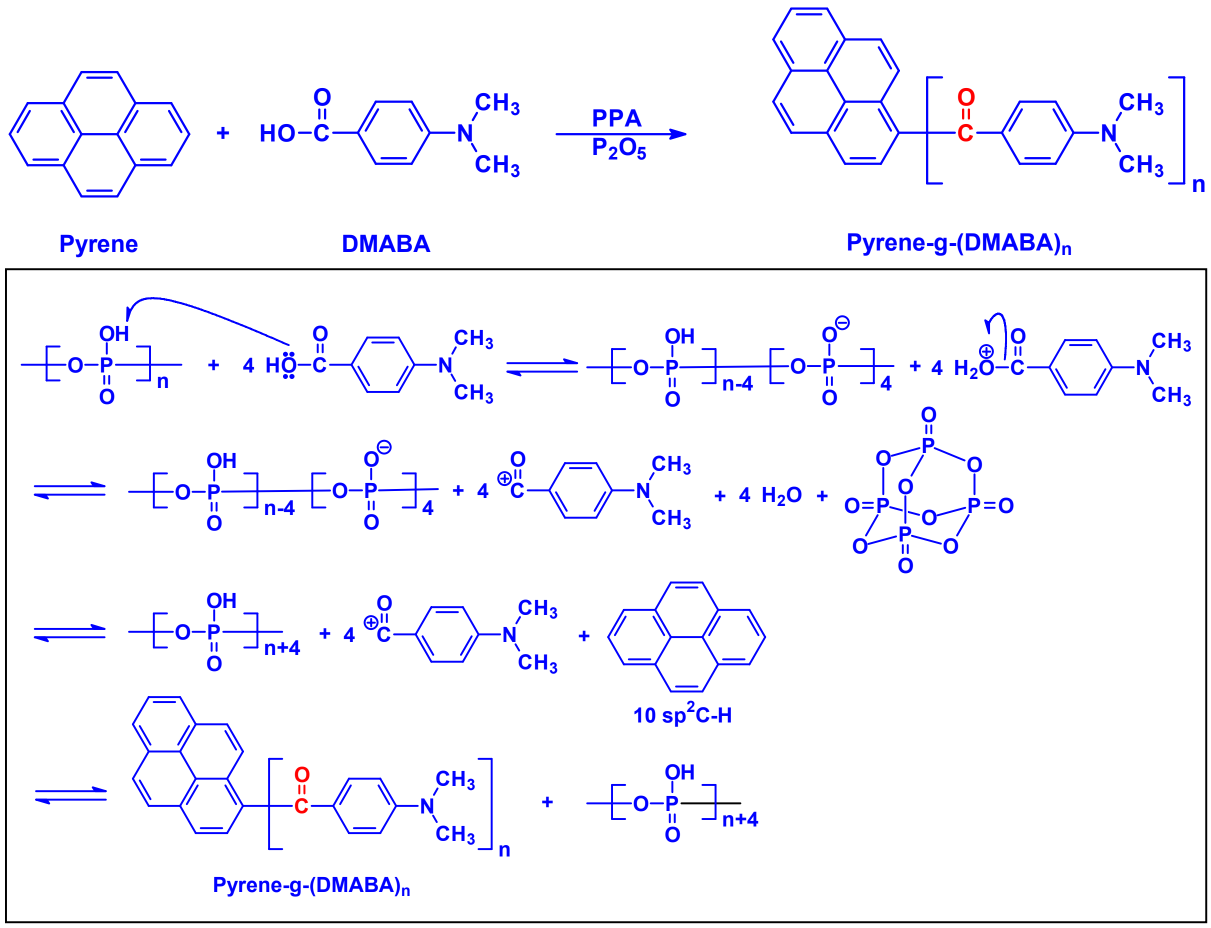

Figure S1. The reaction between pyrene and 4-(N,N-dimethylamino)benzoic acid (DMABA) in polyphosphoric acid (PPA)/phosphorous pentoxide (P_2O_5) (top); proposed mechanism of "direct" Friedel-Crafts acylation reaction between acylium ion ($^+C=O$) of DMABA and sp^2C-H of pyrene.

Pyrene is considered to be a miniature graphene compound. A model reaction between pyrene and 4-(dimethylamino)benzoic acid (DMABA) could give an insight into the edge-chemistry of graphite. Hence, the reaction between pyrene and DMABA was carried under the same conditions as the grafting of *p*PEK onto the edge of graphite in polyphosphoric acid (PPA)/phosphorous pentoxide (P_2O_5).

The proposed mechanism of the electrophilic substitution reaction is a "direct" Friedel-Crafts acylation between the acylium ion (Ph-C^+=O) of DMABA and sp^2C-H of pyrene to give pyrene-g-$(DMABA)_n$. The covalent attachment and number of DMABA can be confirmed by FT-IR and estimated by elemental analysis (EA). The FT-IR spectra of pyrene, DMABA and pyrene-g-$(DMABA)_n$ are presented in Figure S2 and EA results are summarized in Table S1.

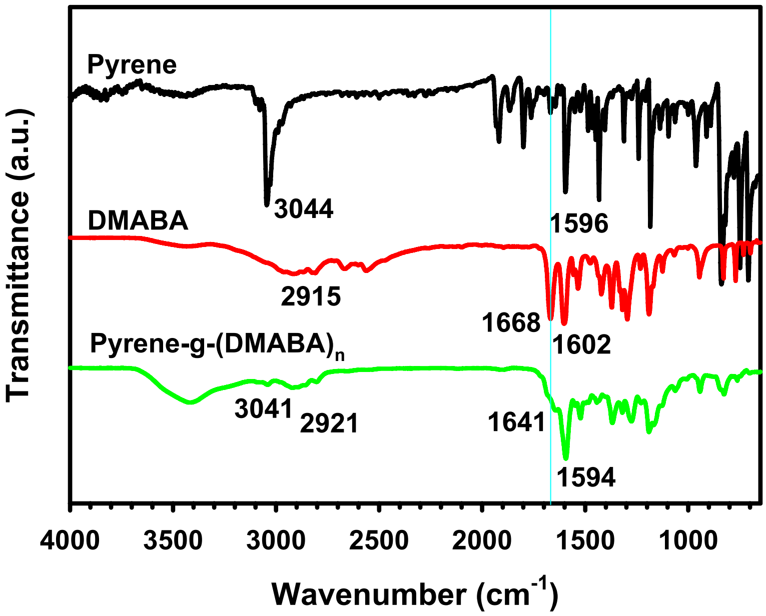

Figure S2. FT-IR (KBr pellet) spectra of pyrene, 4-(dimethylamino)benzoic acid (DMABA) and pyrene-g-(DMABA)$_n$.

To avoid unexpected variables, the resultant pyrene-g-(DMABA)$_n$ was completely worked-up by Soxhlet extraction with water for three days to remove the reaction medium and with hexane for three days to get rid of un-reacted DMABA and low molar mass impurities. The resultant pyrene-g-(DMABA)$_n$ was freeze-dried under reduced pressure (10^{-2} mmHg). FT-IR is a convenient tool to trace chemical bonds in carbon materials. Pyrene shows strong sp^{2}C-H peak at 3044 cm^{-1} (Figure S2, top). DMABA displays a strong carbonyl (C=O) peak from carboxylic acid at 1668 cm^{-1} and sp^{3}C-H peak around 2915 cm^{-1} (Figure S2, middle). Pyrene-g-(DMABA)$_n$ does show a relatively weak sp^{2}C-H and sp^{3}C-H peaks around 3041 and 2921 cm^{-1}, these are due mainly to DMABA. The distinct carbonyl stretching peak of pyrene-g-(DMABA)$_n$ appears at 1641 cm^{-1} (Figure S2, bottom). If there is free standing DMABA in the sample, there must be a trace of the residual benzoic acid carbonyl (C=O) stretching peak at 1668 cm^{-1}. However, pyrene-g-(DMABA)$_n$ does not show the peak, indicating it does not contain residual DMABA impurities. It is evident that a number of DMABA units are covalently bonded to the edges of pyrene, yet the number of DMABA cannot be determined. Nevertheless, the covalent bonding of DMABA to the edge of graphite can be assumed, therefore *p*PEK bonding to the edge of graphite is also likely to have occurred.

Table S1. Empirical formula (EF), formula weight (FW) and elemental analysis of samples

Sample	EF	FW	Elemental Analysis			
			C	H	N	O
Pyrene	$C_{16}H_{10}$	202.25	95.02	4.98	0.00	0.00
Pyrene-g-(DMABA)$_1$	$C_{25}H_{21}N_1O_1$	351.44	85.44	6.02	3.99	4.55
Pyrene-g-(DMABA)$_2$	$C_{34}H_{30}N_2O_2$	498.61	81.90	6.06	5.62	6.42
Pyrene-g-(DMABA)$_3$	$C_{43}H_{39}N_3O_3$	645.89	79.97	6.09	6.51	7.43
Pyrene-g-(DMABA)$_4$	$C_{52}H_{48}N_4O_4$	792.96	78.76	6.10	7.07	8.07
Pyrene-g-(DMABA)$_5$	$C_{61}H_{57}N_5O_5$	940.14	77.93	6.11	7.45	8.51
Pyrene-g-(DMABA)$_6$	$C_{70}H_{66}N_6O_6$	1087.31	77.32	6.12	7.73	8.83
Pyrene-g-(DMABA)$_7$	$C_{79}H_{75}N_7O_7$	1234.48	76.86	6.12	7.94	9.07
Pyrene-g-(DMABA)$_8$	$C_{88}H_{84}N_8O_8$	1381.66	76.50	6.13	8.11	9.26
Pyrene-g-(DMABA)$_9$	$C_{97}H_{93}N_9O_9$	1528.83	76.20	6.13	8.25	9.42
Pyrene-g-(DMABA)$_{10}$	$C_{106}H_{102}N_{10}O_{10}$	1676.01	75.96	6.13	8.36	9.55
Pyrene-g-(DMABA)$_n$	$C_xH_yO_z$	Found	81.78	5.13	4.94	5.63

On the basis of elemental analysis, CHNO contents are 81.78, 5.13, 4.94 and 7.58% for pyrene-g-(DMABA)$_n$. The values are closest to theoretical CHNO values for the empirical formula weight of $C_{34}H_{30}N_2O_2$, which correspond well with those of pyrene-g-(DMABA)$_2$. Hence, disubstitution could be most likely happen to pyrene via "direct" Friedel-Crafts acylation.