Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Excited state electron transfer from aminopyrene to graphene: a combined experimental and theoretical study

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Ground state optimized structures.

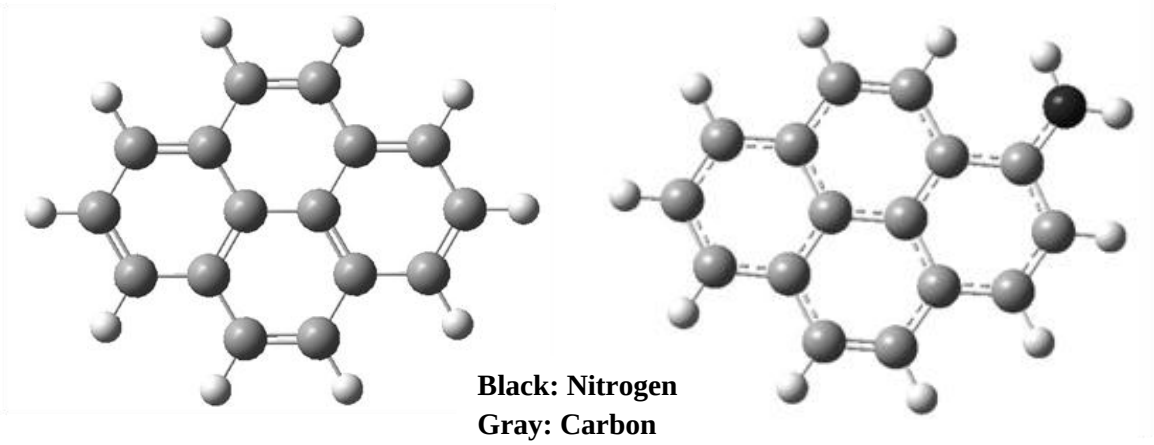
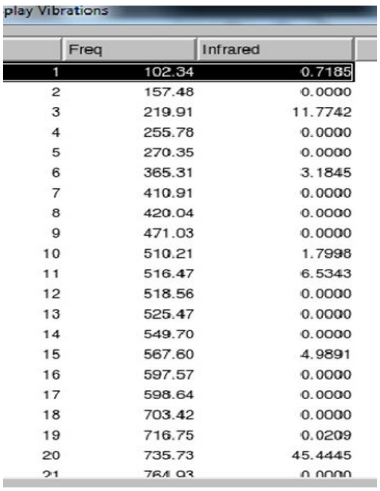


Figure S1. Ground state optimized structures of Pyrene and 1-Aminopyrene (1-Ap).

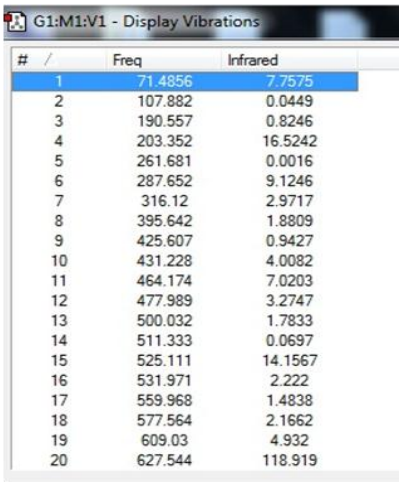
Vibrational frequencies.



play Vibrations

	Freq	Infrared
1	102.34	0.7185
2	157.48	0.0000
3	219.91	11.7742
4	255.78	0.0000
5	270.35	0.0000
6	365.31	3.1845
7	410.91	0.0000
8	420.04	0.0000
9	471.03	0.0000
10	510.21	1.7998
11	516.47	6.5343
12	518.56	0.0000
13	525.47	0.0000
14	549.70	0.0000
15	567.60	4.9891
16	597.57	0.0000
17	598.64	0.0000
18	703.42	0.0000
19	716.75	0.0209
20	735.73	45.4445
21	764.93	0.0000

Pyrene



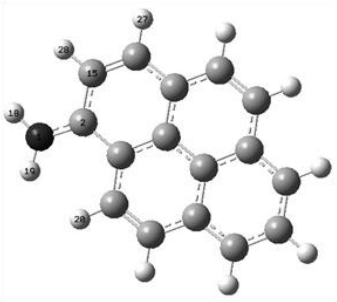
G1:M1:V1 - Display Vibrations

#	Freq	Infrared
1	71.4856	7.7575
2	107.882	0.0449
3	190.557	0.8246
4	203.352	16.5242
5	261.681	0.0016
6	287.652	9.1246
7	316.12	2.9717
8	395.642	1.8809
9	425.607	0.9427
10	431.228	4.0082
11	464.174	7.0203
12	477.989	3.2747
13	500.032	1.7833
14	511.333	0.0697
15	525.111	14.1567
16	531.971	2.222
17	559.968	1.4838
18	577.564	2.1662
19	609.03	4.932
20	627.544	118.919

1-Aminopyrene

Figure S2. Calculated vibrational frequencies for Pyrene and 1-Aminopyrene.

Structural geometry of 1-Ap.



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1-AP
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Symbolic Z-matrix:
Charge =  1 Multiplicity = 2
N
C
C                    1    B1
C                    2    B2       1    A1
C                    3    B3       2    A2       1    D1       0
C                    4    B4       3    A3       2    D2       0
C                    5    B5       4    A4       3    D3       0
C                    6    B6       5    A5       4    D4       0
C                    7    B7       6    A6       5    D5       0
C                    8    B8       7    A7       6    D6       0
C                    9    B9       8    A8       7    D7       0
C                    10   B10      9    A9       8    D8       0
C                    11   B11      10   A10      9    D9       0
C                    12   B12      11   A11      10   D10      0
C                    13   B13      12   A12      11   D11      0
C                    14   B14      13   A13      12   D12      0
C                    13   B15      12   A14      11   D13      0
C                    6    B16      5    A15      4    D14      0
H                    1    B17      2    A16      15   D15      0
H                    1    B18      2    A17      15   D16      0
H                    4    B19      3    A18      2    D17      0
H                    5    B20      4    A19      3    D18      0
H                    7    B21      6    A20      5    D19      0
H                    8    B22      7    A21      6    D20      0
H                    9    B23      8    A22      7    D21      0
H                    11   B24      10   A23      9    D22      0
H                    12   B25      11   A24      10   D23      0
H                    14   B26      13   A25      12   D24      0
H                    15   B27      14   A26      13   D25      0
```

Variables:

B1	1.37396	B18	1.01014	A9	122.11664	D7	0.
B2	1.43029	B19	1.08775	A10	120.9007	D8	-180.
B3	1.43822	B20	1.08828	A11	121.46536	D9	179.99731
B4	1.36827	B21	1.08828	A12	122.41968	D10	0.
B5	1.43849	B22	1.0879	A13	121.41258	D11	-179.99534
B6	1.41002	B23	1.08832	A14	119.32038	D12	179.98923
B7	1.39812	B24	1.08813	A15	118.37837	D13	0.
B8	1.39824	B25	1.08899	A16	119.98855	D14	0.00589
B9	1.41048	B26	1.08875	A17	123.03817	D15	0.03591
B10	1.44021	B27	1.08845	A18	119.78924	D16	-179.96261
B11	1.36821	A1	122.14989	A19	120.26591	D17	-0.01427
B12	1.43626	A2	122.60231	A20	119.13181	D18	-180.
B13	1.41066	A3	121.77326	A21	119.70058	D19	0.
B14	1.38748	A4	121.33136	A22	120.15815	D20	-180.
B15	1.43264	A5	122.26559	A23	118.39314	D21	-180.
B16	1.43392	A6	120.5873	A24	120.39921	D22	0.
B17	1.01265	A7	120.6363	A25	119.08306	D23	-180.
		A8	120.83988	A26	119.98819	D24	-0.00883
				D1	-0.01447	D25	-179.99646
				D2	179.98449		
				D3	0.		
				D4	-179.99528		
				D5	-180.		
				D6	0.		

Figure S3. Optimized structural geometry of 1-Ap in Cartesian coordinates.

FESEM images.

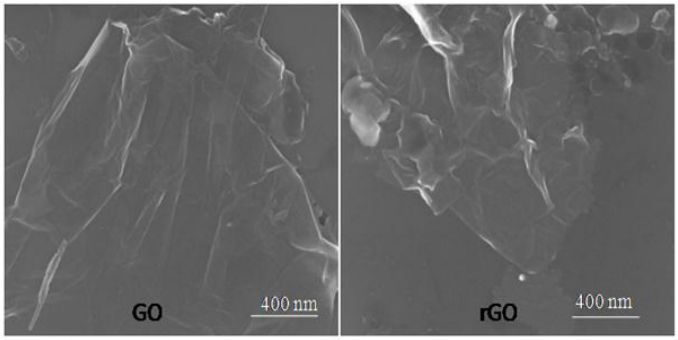

Figure S4. Field emission scanning electron microscopic images of GO and rGO dispersions.

Raman spectra.

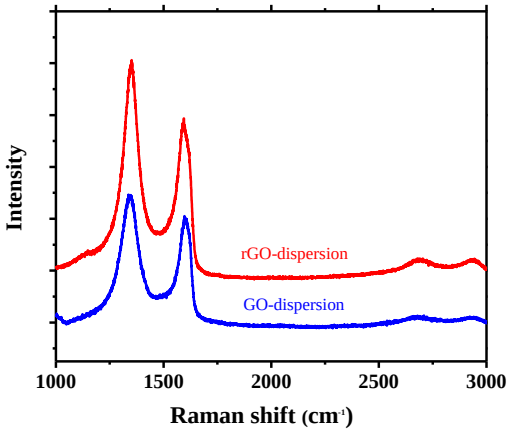

Figure S5. Raman spectra of GO and rGO dispersions.

Fluorescence decay.

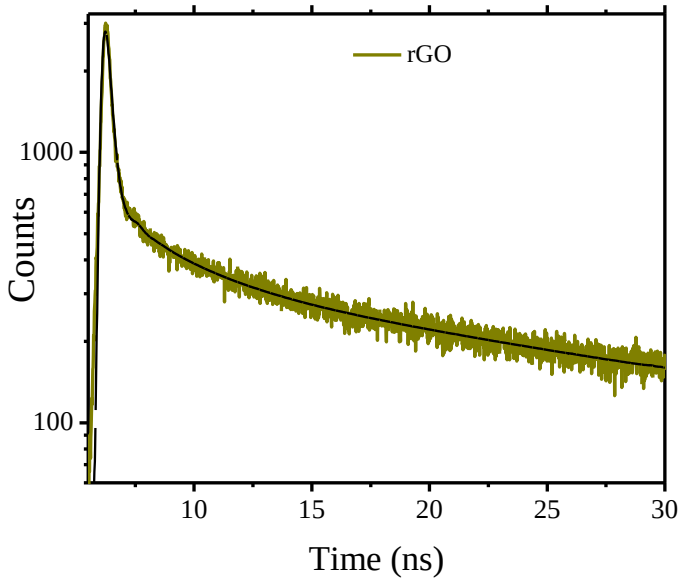

Figure S6. Time-resolved fluorescence decay profile of rGO with excitation at 441 nm (solid curve is the fitting result).

Cyclic voltammetry.

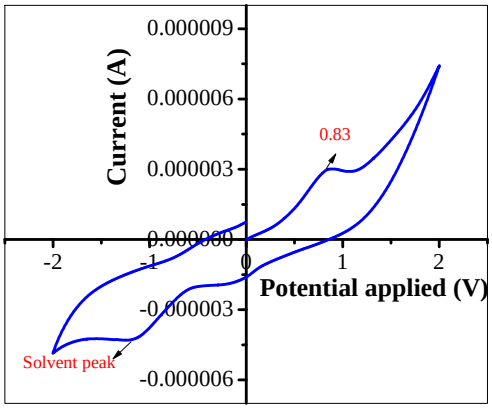

Figure S7. Cyclic voltammogram of 1-Ap in water-THF (99:1) mixed solvent.

Finding the S_1 state energy (E_{00}) for 1-Ap.

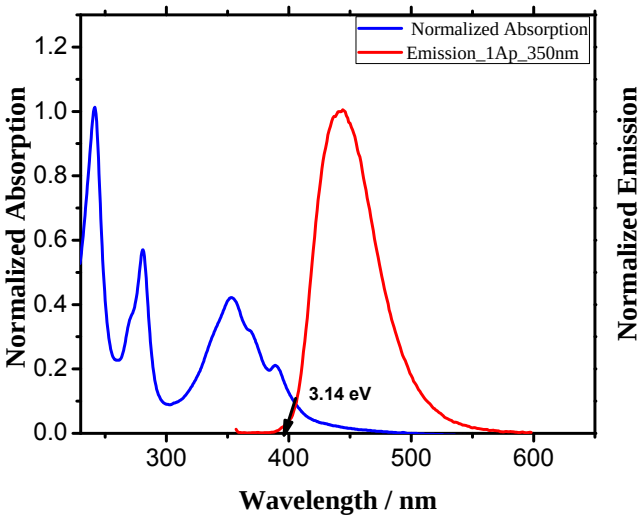

Figure S8. Normalized absorption and fluorescence spectra of 1-Ap showing the energy of the S_1 state (E_{00}).

Finding molecular weight of graphene.

Molecular weight of a circular graphene sheet can be estimated by covering all the carbon atoms by a circular arc with radius r (**Figure S9**).

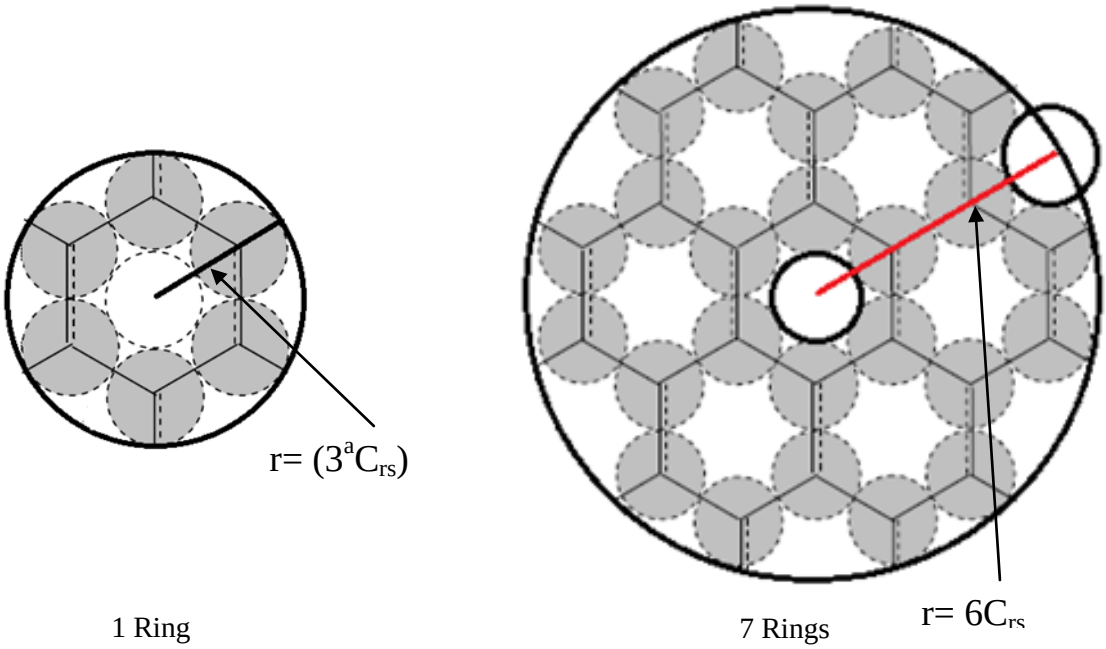

Figure S9. Circular graphene sheet enclosed by a circle of radius r.
[a]C_{rs} = Carbon resonance bond radius in graphene structure, ~ 0.71 (1.42/2) Å

We can see from the above figure (S5) that the number of carbon atoms in a sheet varies with the square of the radius (r^2) of the sheet,

$$N \propto r^2.$$

This implies that a 100 nm circular graphene sheet can contain 15×10^5 carbon atoms. Therefore, the sheet has a molecular weight of 18×10^6 gm.

Vertical transition energies of 1-Ap.

Few specific transitions of 1-Ap having reasonably high oscillator strengths obtained by TD-DFT along with the assignment of the contributions from different molecular orbitals are shown in Table I.

Table I. Vertical transition energies for 1-Ap

Compound	λ_{max} (nm)	Oscillator strength	Assignment
1-Ap	378.61	0.4183	H[a]->L[b] (76%), H-1->L+1 (5%).
	346.75	0.0550	H-1->L (12%), H->L+1 (78%), H-2->L (2%).
	311.30	0.0376	H->L+2 (88%), H-1->L (5%).
	276.61	0.2443	H-1->L (67%), H->L+1 (8%), H->L+2 (2%), H->L+3 (5%).
	258.10	0.0325	H-2->L (64%), H-1->L+1 (13%), H->L+3 (11%), H-3->L (3%).

[a]*Highest occupied molecular orbital*
[b]*Lowest unoccupied molecular orbital*