Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information:

Ground and excited states of Naphthalene-Water (Naphtha-W_6) Clusters: A Computational Study

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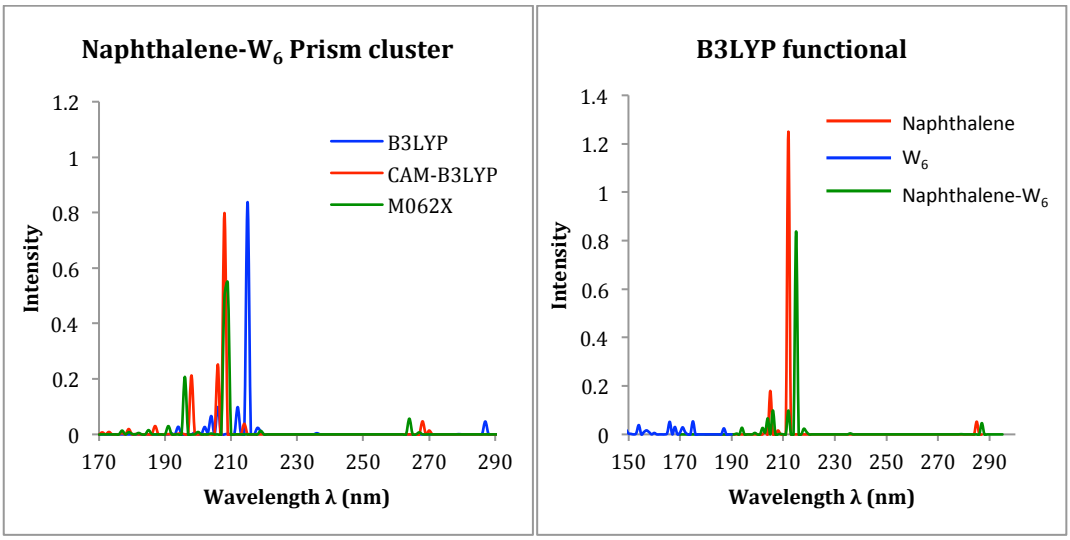
Table S1. List of lowest energy singlet electronic transitions obtained using TD-B3LYP, TD-CAM-B3LYP and TD-M06-2X functionals on MP2 optimized naphtha-W_6 prism shaped clusters using aug-cc-pVTZ basis set. (Value in parenthesis correspond to singlet $\pi \rightarrow \pi^*$ transitions of an isolated naphthalene molecule).

DFT functional	**E (eV)**	**λ (nm)**	**Oscillator strength *(f)***	**Character**
B3LYP	4.17 (4.21)	297.2 (294.9)	0.0481 (0.0544)	$\pi \rightarrow \pi^*$
	4.32 (4.32)	287.3 (286.8)	0.0007 (0.0000)	$\pi \rightarrow \pi^*$
	5.61 (5.72)	221.0 (216.7)	0.5259 (1.2356)	$\pi \rightarrow \pi^*$
	5.61	221.0	0.2916	$\pi \rightarrow \pi^*$ (Diffuse)
	5.72	216.7	0.1322	$\pi \rightarrow \pi^*$
	5.91	209.8	0.1408	$\pi \rightarrow \pi^*$
	6.03	205.5	0.0182	Naphtha-Diffuse State
	6.08	204.1	0.0197	Naphtha-CT state
	6.36	195.1	0.0137	Water-CT state
CAM-B3LYP	4.45 (4.47)	278.9 (277.4)	0.0407 (0.0000)	$\pi \rightarrow \pi^*$
	4.47 (4.49)	277.2 (276.2)	0.0223 (0.0708)	$\pi \rightarrow \pi^*$
	5.83 (5.90)	212.5 (210.1)	0.7522 (1.3105)	$\pi \rightarrow \pi^*$
	6.16	201.3	0.2063	$\pi \rightarrow \pi^*$
	5.76	215.2	0.1769	$\pi \rightarrow \pi^*$
	5.90	210.2	0.1395	$\pi \rightarrow \pi^*$ (Diffuse)
	6.63	187.1	0.0261	Naphtha-Diffuse State
	6.84	181.3	0.0145	Naphtha-CT state
	6.87	180.4	0.0001	Water-CT state
M06-2X	4.50 (4.52)	275.7 (274.2)	0.0365 (0.0000)	$\pi \rightarrow \pi^*$
	4.52 (4.55)	274.1 (272.4)	0.0287 (0.0721)	$\pi \rightarrow \pi^*$
	5.82 (5.89)	213.1 (210.4)	0.8799 (1.2696)	$\pi \rightarrow \pi^*$
	6.21	199.5	0.2068	$\pi \rightarrow \pi^*$
	5.88	210.7	0.1236	$\pi \rightarrow \pi^*$
	6.54	190.0	0.0264	Naphtha-Diffuse State
	6.82	181.2	0.0096	Naphtha-CT state
	6.95	178.4	0.0143	Naphtha-CT state

Table S2. List of lowest energy singlet electronic transitions obtained using TD-B3LYP, TD-CAM-B3LYP and TD-M06-2X functionals on MP2 optimized naphtha-W_6 cage shaped clusters using aug-cc-pvTZ basis set. (Value in parenthesis correspond to singlet $\pi \rightarrow \pi^*$ transitions of an isolated naphthalene molecule).

DFT functional	**E (eV)**	**λ (nm)**	**Oscillator strength *(f)***	**Electronic transition**
B3LYP	4.20 (4.21)	295.4 (294.9)	0.0497 (0.0544)	$\pi \rightarrow \pi^*$
	4.31 (4.32)	287.5 (286.8)	0.0008 (0.0000)	$\pi \rightarrow \pi^*$
	5.65 (5.72)	219.2 (216.7)	0.7406 (1.2356)	$\pi \rightarrow \pi^*$
	5.74	215.9	0.1735	Naphtha-CT state
	5.90	210.3	0.1502	$\pi \rightarrow \pi^*$
	5.8732	211.1	0.0375	Naphtha-Diffuse state
	5.7193	216.8	0.0761	Naphtha-CT state
	6.12	202.5	0.0104	Naphtha-CT state
CAM-B3LYP	4.46 (4.47)	278.2 (277.4)	0.0091 (0.0000)	$\pi \rightarrow \pi^*$
	4.49 (4.49)	276.3 (276.2)	0.0560 (0.0698)	$\pi \rightarrow \pi^*$
	5.86 (5.90)	211.5 (210.1)	1.0999 (1.3105)	$\pi \rightarrow \pi^*$
	6.13	202.26	0.2181	$\pi \rightarrow \pi^*$
	5.81	213.35	0.0337	$\pi \rightarrow \pi^*$ (Diffuse)
	6.40	193.7	0.0193	Naphtha-CT state
	6.93	179.0	0.0018	Water-CT state
M06-2X	4.51 (4.52)	275.0 (274.2)	0.0078 (0.0000)	$\pi \rightarrow \pi^*$
	4.55 (4.55)	272.7 (272.4)	0.0599 (0.0721)	$\pi \rightarrow \pi^*$
	5.85 (5.89)	212.0 (210.4)	0.9408 (1.2696)	$\pi \rightarrow \pi^*$
	6.18	200.5	0.2135	$\pi \rightarrow \pi^*$
	5.79	214.17	0.0366	Naphtha-Diffuse state
	6.29	197.25	0.0222	Naphtha-CT state
	6.75	183.7	0.0022	Water-CT state



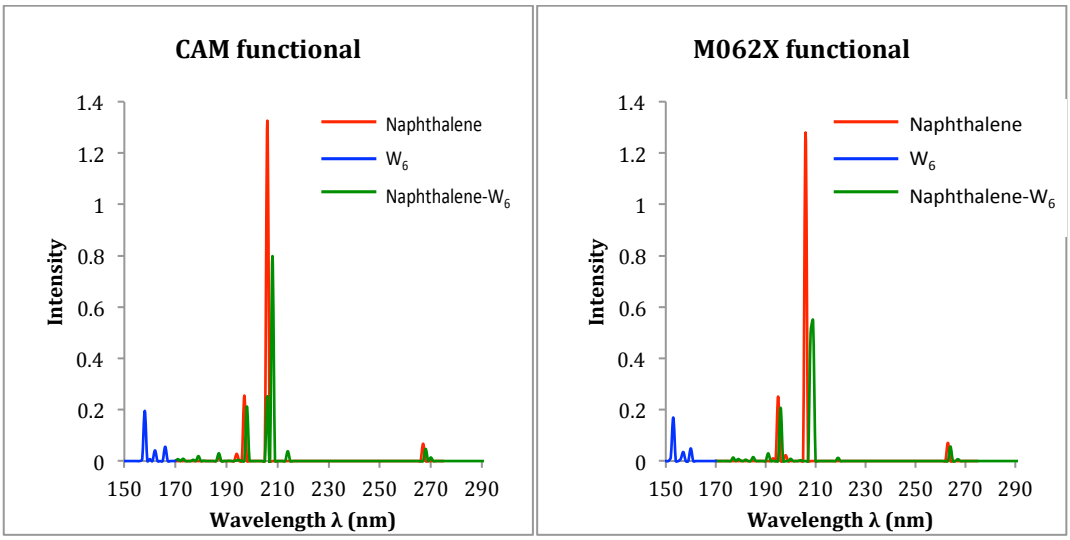


Figure S1. Simulated UV spectra obtained from TD-DFT calculations on wB97XD optimized ground state geometries of prism shaped water W_6 cluster, Naphthalene-W_6 cluster and Naphthalene. (a) Comparison of B3LYP, CAM-B3LYP and M06-2X functionals performance on Naphthalene-W_6 prism cluster (b) Performance of B3LYP functional (c) Performance of CAM-B3LYP functional (d) Performance of M06-2X functional.

Table S3. List of lowest energy $\pi \rightarrow \pi^*$ singlet electronic transitions and important electronic transitions corresponding to highest peak intensities (or oscillator strengths) obtained using B3LYP, CAM-B3LYP and M06-2X hybrid functional on wB97XD optimized naphthalene-W_6 prism shaped clusters. (Value in parenthesis correspond to singlet $\pi \rightarrow \pi^*$ transitions of an isolated naphthalene molecule).

DFT functional	**E (eV)**	**λ (nm)**	**Oscillator strength *(f)***	**Electronic transition**
B3LYP	4.33 (4.35)	286.6 (284.8)	0.0466 (0.0527)	$\pi \rightarrow \pi^*$
	4.45 (4.45)	278.8 (278.8)	0.0009 (0.0000)	$\pi \rightarrow \pi^*$
	5.76 (5.84)	215.3 (212.2)	0.8379 (1.2499)	$\pi \rightarrow \pi^*$
	5.25	236.0	0.0043	Naphtha- CT state
	5.84	212.2	0.0986	$\pi \rightarrow \pi^*$ (Diffused)
	6.01	206.4	0.0988	$\pi \rightarrow \pi^*$
	6.07	204.4	0.0663	Naphtha- CT state
	6.41	193.5	0.0019	Naphtha- Diffused State
	6.47	191.5	0.0033	Naphtha- Diffused State
	6.38	194.4	0.0076	Water CT state
CAM-B3LYP	4.60 (4.61)	269.7 (269.3)	0.0139 (0.0000)	$\pi \rightarrow \pi^*$
	4.63 (4.65)	267.5 (266.5)	0.0472 (0.0675)	$\pi \rightarrow \pi^*$
	5.79	214.2	0.0383	Naphtha- CT state
	5.96 (6.03)	207.9 (205.7)	0.7986 (1.3260)	$\pi \rightarrow \pi^*$
	6.01	206.34	0.2524	$\pi \rightarrow \pi^*$
	6.28	197.5	0.2126	$\pi \rightarrow \pi^*$
	7.02	176.75	0.0031	Naphtha- Diffused State
	7.16	173.26	0.0089	Naphtha- CT state
	7.25	171.06	0.0072	Naphtha- Diffused State
M06-2X	4.64 (4.66)	266.9 (266.3)	0.0072 (0.0000)	$\pi \rightarrow \pi^*$
	4.69 (4.72)	264.1 (262.5)	0.0568 (0.0708)	$\pi \rightarrow \pi^*$
	5.66	219.1	0.0127	$\pi \rightarrow \pi^*$
	5.93 (6.02)	208.9 (206.1)	0.5453 (1.2799)	$\pi \rightarrow \pi^*$
	5.98	207.5	0.4962	$\pi \rightarrow \pi^*$
	6.34	195.7	0.2076	$\pi \rightarrow \pi^*$
	6.92	179.2	0.0078	Naphtha- CT state

	7.01	176.8	0.0137	Naphtha- CT state

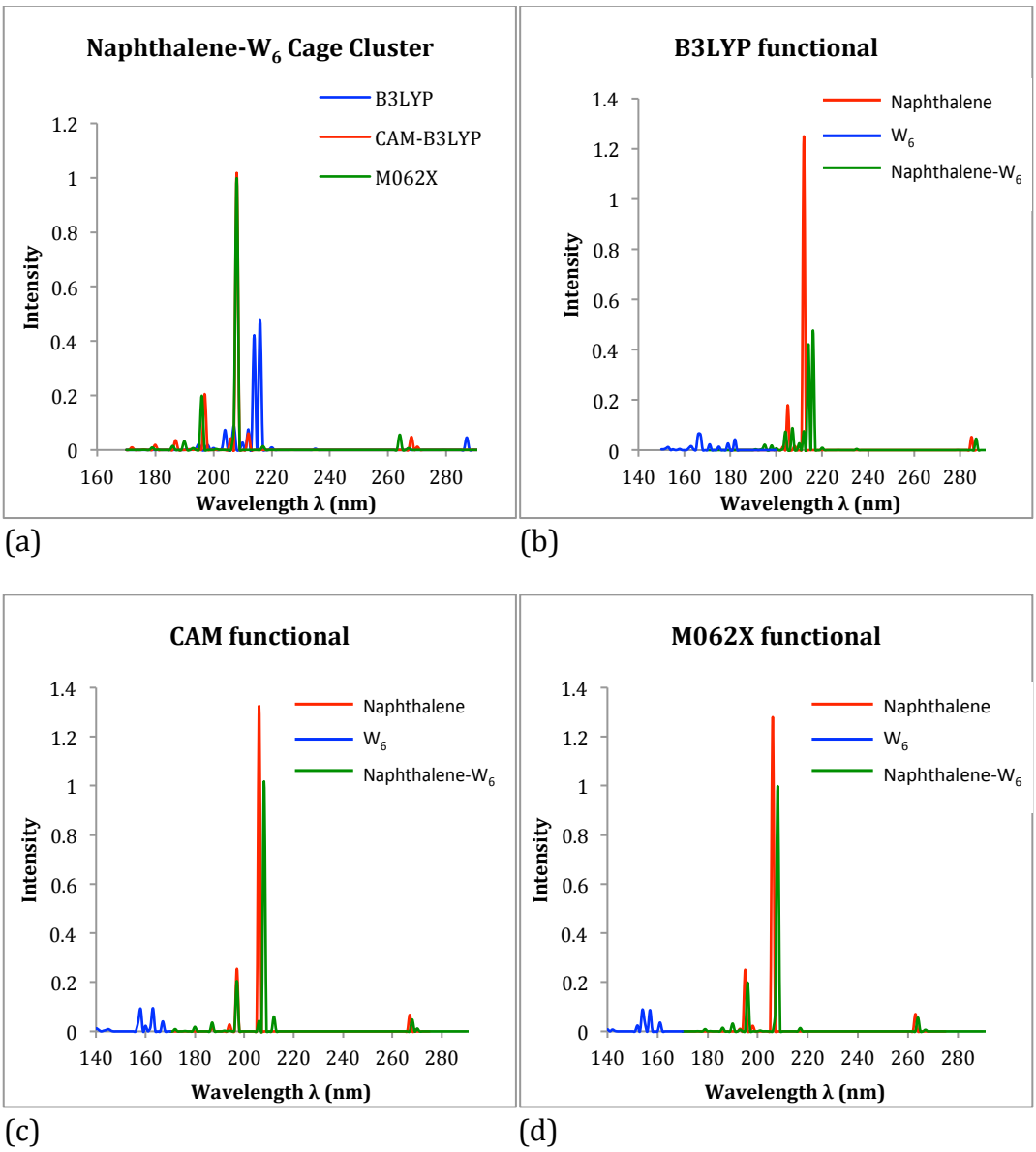


Figure S2. Simulated UV spectra obtained from TD-DFT calculations on wB97XD optimized ground state geometries of prism shaped water W_6 cluster, Naphthalene-W_6 cluster and Naphthalene. (a) Comparison of B3LYP, CAM-B3LYP and M06-2X functionals performance on Naphthalene-W_6 cage cluster (b) Performance of B3LYP functional (c) Performance of CAM-B3LYP functional (d) Performance of M06-2X functional.

Table S4. List of lowest energy $\pi \rightarrow \pi^*$ singlet electronic transitions and important electronic transitions corresponding to highest peak intensities (or oscillator strengths) obtained using B3LYP, CAM-B3LYP and M06-2X hybrid functional on wB97XD optimized naphthalene-W_6 cage shaped clusters. (Value in parenthesis correspond to singlet $\pi \rightarrow \pi^*$ transitions of an isolated naphthalene molecule).

DFT functional	**E (eV)**	**λ (nm)**	**Oscillator strength *(f)***	**Electronic transition**
B3LYP	4.32 (4.35)	286.7 (284.8)	0.0461 (0.0527)	$\pi \rightarrow \pi^*$
	4.44 (4.45)	279.0 (278.8)	0.0004 (0.0000)	$\pi \rightarrow \pi^*$
	5.73 (5.84)	216.3 (212.2)	0.4748 (1.2499)	$\pi \rightarrow \pi^*$
	5.79	214.3	0.4217	$\pi \rightarrow \pi^*$
	5.86	211.8	0.0756	Naphtha-Diffused State
	5.99	206.7	0.0881	Naphtha- CT state
	6.40	193.6	0.0057	Naphtha- CT state
	6.41	193.4	0.0015	Naphtha-Diffused State
	6.48	191.5	0.0031	Water- CT state
	5.27	235.3	0.0043	Naphtha- CT state
CAM-B3LYP	4.59 (4.60)	269.7 (269.3)	0.0118 (0.0000)	$\pi \rightarrow \pi^*$
	4.63 (4.65)	267.7 (266.5)	0.0483 (0.0675)	$\pi \rightarrow \pi^*$
	5.97 (6.03)	207.7 (205.7)	1.0179 (1.3260)	$\pi \rightarrow \pi^*$
	5.84	212.4	0.0607	Naphtha- CT state
	6.03	205.7	0.0429	Naphtha-Diffused State
	6.28	197.4	0.2053	$\pi \rightarrow \pi^*$
	7.21	172.0	0.0070	Naphtha- CT state
	7.23	171.5	0.0024	Naphtha-Diffused State
	7.04	176.1	0.0009	Naphtha-Diffused State
M06-2X	4.65 (4.66)	266.9 (266.3)	0.0066 (0.0000)	$\pi \rightarrow \pi^*$
	4.69 (4.72)	264.1 (262.5)	0.0563 (0.0708)	$\pi \rightarrow \pi^*$
	5.95 (6.02)	208.3 (206.1)	0.9985 (1.2799)	$\pi \rightarrow \pi^*$
	5.99	206.9	0.0790	$\pi \rightarrow \pi^*$ (Diffused)
	6.34	195.6	0.1991	$\pi \rightarrow \pi^*$
	6.68	185.6	0.0141	Naphtha-Diffused State

	6.93	178.9	0.0092	Naphtha- CT state
	7.03	176.3	0.0007	Naphtha- Diffused State

Table S4. List of lowest energy $\pi \rightarrow \pi^*$ singlet electronic transitions and important electronic transitions corresponding to highest peak intensities (or oscillator strengths) obtained using B3LYP, CAM-B3LYP and M06-2X hybrid functional on MP2 optimized naphthalene-W_6 cage shaped clusters. (Value in parenthesis correspond to singlet $\pi \rightarrow \pi^*$ transitions of an isolated naphthalene molecule).

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	5.73 (5.84)	216.3 (212.2)	0.4748 (1.2499)	$\pi \rightarrow \pi^*$
	5.79	214.3	0.4217	$\pi \rightarrow \pi^*$
	5.86	211.8	0.0756	Naphtha-Diffused State
	5.99	206.7	0.0881	Naphtha- CT state
	6.40	193.6	0.0057	Naphtha- CT state
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	4.63 (4.65)	267.7 (266.5)	0.0483 (0.0675)	$\pi \rightarrow \pi^*$
	5.97 (6.03)	207.7 (205.7)	1.0179 (1.3260)	$\pi \rightarrow \pi^*$
	5.84	212.4	0.0607	Naphtha- CT state
	6.03	205.7	0.0429	Naphtha-Diffused State
	6.28	197.4	0.2053	$\pi \rightarrow \pi^*$
	7.21	172.0	0.0070	Naphtha- CT state
	7.23	171.5	0.0024	Naphtha-Diffused State
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	4.69 (4.72)	264.1 (262.5)	0.0563 (0.0708)	$\pi \rightarrow \pi^*$
	5.95 (6.02)	208.3 (206.1)	0.9985 (1.2799)	$\pi \rightarrow \pi^*$
	5.99	206.9	0.0790	$\pi \rightarrow \pi^*$

				(Diffused)
	6.34	195.6	0.1991	$\pi \rightarrow \pi^*$
	6.68	185.6	0.0141	Naphtha-Diffused State
	6.93	178.9	0.0092	Naphtha- CT state
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