Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information for:

Naphthalene bisimide asymmetrically and symmetrically N-substituted with triarylamine – comparison of spectroscopic, electrochemical, electronic and self-assembly properties

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1. Synthetic procedures

1.1. Synthetic procedure of *N,N*-di(4-butylphenyl)-1,4-phenylenediamine and NBI-$(TAA)_2$ was described in detail in the literature.[1-2]

1.1.1. Synthesis of *N,N*-di(4-butylphenyl)-1,4-phenylenediamine (1)

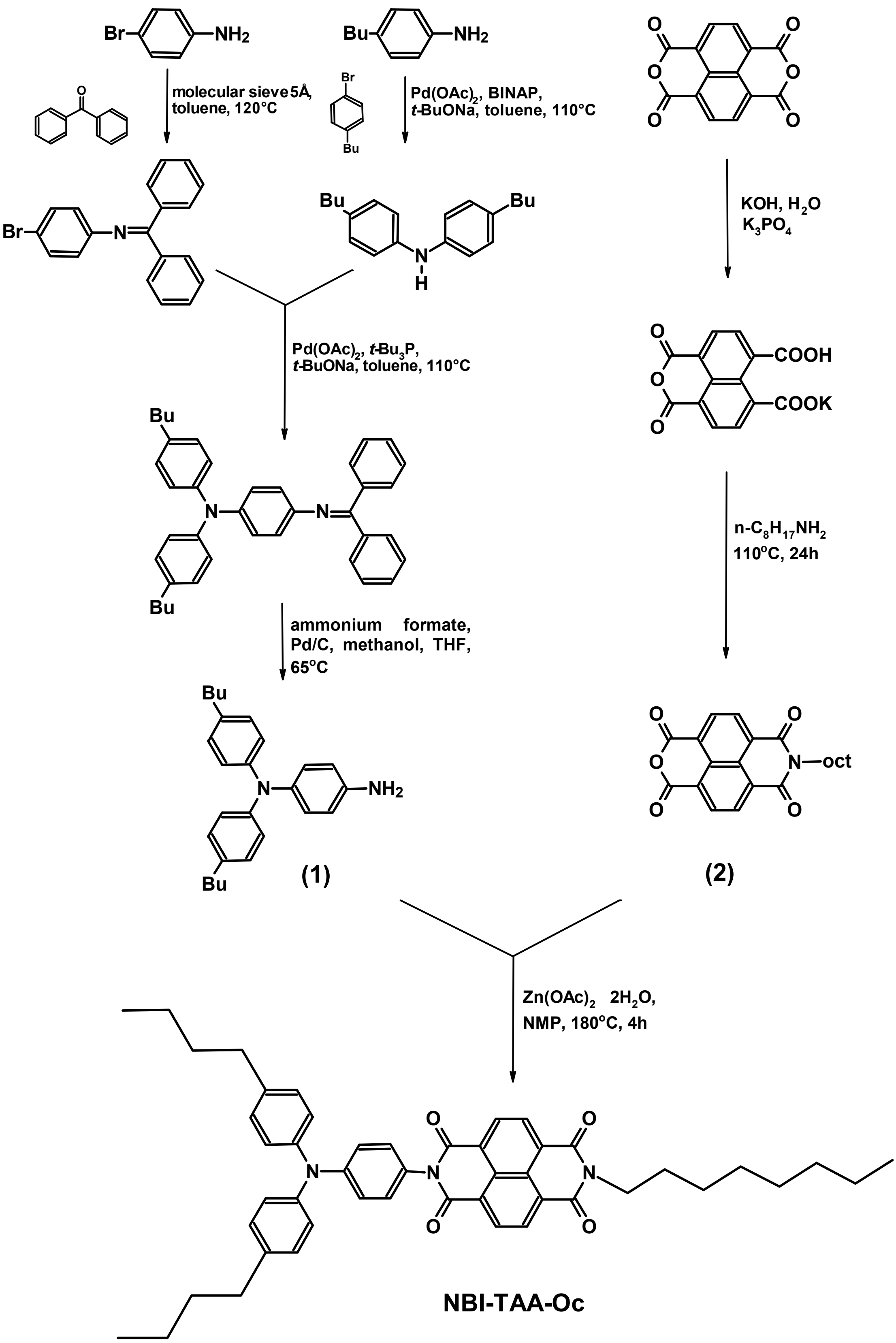
The crude product was obtained as brown oil (3,34 g, 96 % reaction yield).

1.1.2. Synthesis of *N,N'*-bis{4-[bis(4-butylphenyl)-amino]phenyl}-1,4,5,8-naphthalenetetra-carboxylic -1,4:5,8-bisimide (NBI-$(TAA)_2$).

NBI-$(TAA)_2$ was prepared in a form of a violet solid with the reaction yield of 57%.

1.2. Synthesis of N-{4-[bis(4-butylphenyl)-amino]phenyl }-N'-octyl-1,4,5,8-naphthalene-tetracarboxylic -1,4:5,8-bisimide (NBI-TAA-Oc)

NBI-TAA-Oc was prepared using the reaction sequence depicted in *Scheme 1*.


Br
NH_2
Bu
NH_2
molecular sieve 5Å, toluene, 120°C
Br
Bu
$Pd(OAc)_2$, BINAP, t-BuONa, toluene, 110°C
KOH, H_2O
K_3PO_4
Br
N
Bu
Bu
N
H
$Pd(OAc)_2$, t-Bu_3P, t-BuONa, toluene, 110°C
COOH
COOK
Bu
N
N
Bu
n-$C_8H_{17}NH_2$
110°C, 24h
ammonium formate, Pd/C, methanol, THF, 65°C
Bu
N
NH_2
Bu
(1)
N—oct
(2)
$Zn(OAc)_2$ $2H_2O$, NMP, 180°C, 4h
N
N
N
NBI-TAA-Oc

Scheme 1

1.2.1. N-octyl-1,4,5,8-naphthalenetetracarboxylic-1,8-anhydride-4,5-imide (2).

Following the procedure from the literature[3-4] 1,4,5,8-naphthalenetetracarboxylic dianhydride (2.0 g, 7.5mmol), water (350mL) and KOH (1.0M, 65ml)were stirred to dissolve (for around 0.5 h). After the starting material had dissolved, the solution was acidified to pH 6.4 with H_3PO_4 (1.0 M). Octylamine (1.0 g, 7.5 mmol) was added and the solution was refluxed at 110°C for one day. The solution was filtered, and the filtrate acidified with acetic acid (50%). The precipitate was collected by vacuum filtration, washed with water and dried in vacuum at 100°C. The crude product was extracted with acetone in a Soxhlet apparatus during one day to yield 40% (0.80 g) as a light-brown powder.

^{1}H NMR (DMSO, 400 MHz): 8.50 (d, J = 7.6 Hz, 2 H), 8.07 (d, J = 7.6 Hz, 2H), 4.02 (t, J = 7.4 Hz, 2H), 1.67-1.58 (m, 2H), 1.36-1.18(m, 10H), 0.84 (d, J = 6.8 Hz, 3H);

1.2.2. Synthesis of the NBI-TAA-Oc *via* condensation reaction between *N,N*-di(4-butylphenyl)-1,4-phenylenediamine and octyl monosubstituted naphthalene bisimides.

0.3 g (0.81 mmol) of N,N'-di(4-butylphenyl)-1,4-phenylenediamine (1) and 0.18 g (0.81 mmol) of zinc acetate dihydrate were added to a stirred suspension of 0.81 mmol of naphthalene (0.31 g) monoanhydride in 10 ml of dry 1-methyl-2-pyrrolidinone (NMP). The resulting mixture was stirred at 180°C for 4 hours under argon atmosphere, and then poured into 50 ml of cold water. The obtained precipitate was filtered off, washed with water and acetone, dried in a desiccator. The obtained bisimides were purified using a chromatographic column (silica gel, and the following eluents: methylene chloride: ethyl acetate (1:1 v/v). The crude product was dissolved in chloroform and precipitated with acetone, while cooling. The obtained solid was filtered off, washed with acetone and dried. NBI-TAA-Oc was prepared in a form of a violet solid with the reaction yield of 76%.

^{1}H NMR ($CDCl_3$, 400 MHz): 8.79 (s, 4H); 7.16-7.07 (m, 12H), 4.21 (t, J= 7.6 Hz, 2H), 2.58 (t, J= 7.8 Hz, 4H); 1.80-1.71 (m, 2H); 1.65-1.54 (m, 4H), 1.47-1.23 (m, 16H); 0,94 (t, J=7.4 Hz, 6H), 0,88 (t, J=7.0 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz):163.2; 162.8; 148.7; 144.9; 138.4; 131.2; 131.0; 129.3; 128.7; 126.9; 126.8; 126.7; 126.6; 125.3; 121.5; 41.0; 35.1; 33.7; 31.8; 29.3; 29.2; 27.1; 22.6; 22.4; 14.1; 13.9. **FTIR (KBr, cm^{-1}):** 3384, 3027, 2956, 2926, 2856, 1708, 1667, 1601, 1579, 1506, 1451, 1372, 1346, 1320, 1282, 1245, 1189, 1138, 1088, 976, 880, 825, 768, 729. **UV-vis** ($CHCl_3$): λ_{max}= 303 nm, 342 nm, 360 nm, 381 nm.

Elemental analysis: Calcd for $C_{48}H_{51}N_3O_4$: C, 78.58, H, 6.96, N, 5.73. Found: C, 78.48, H, 6.99, N, 5.72.

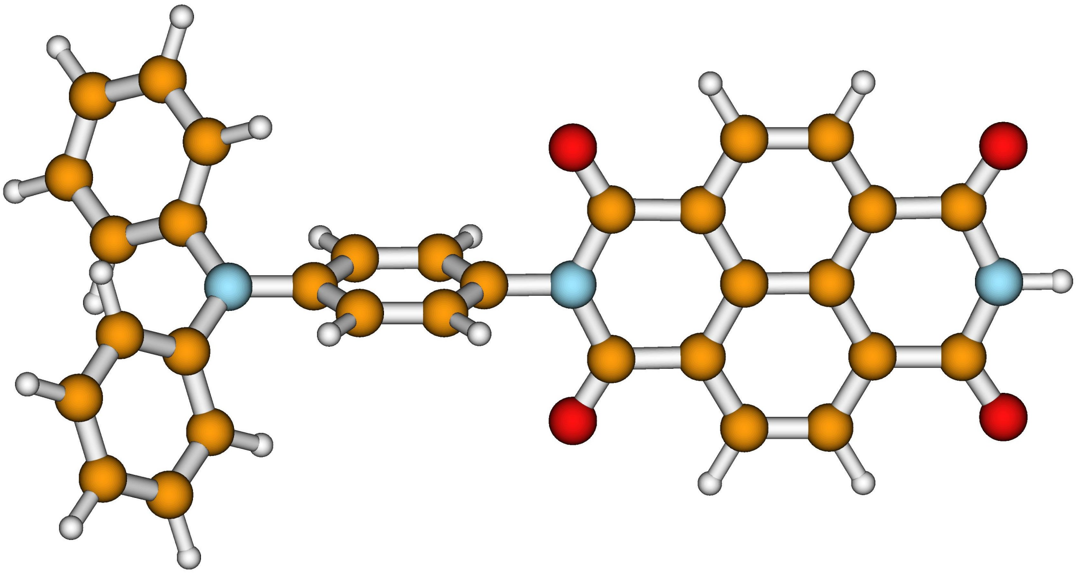
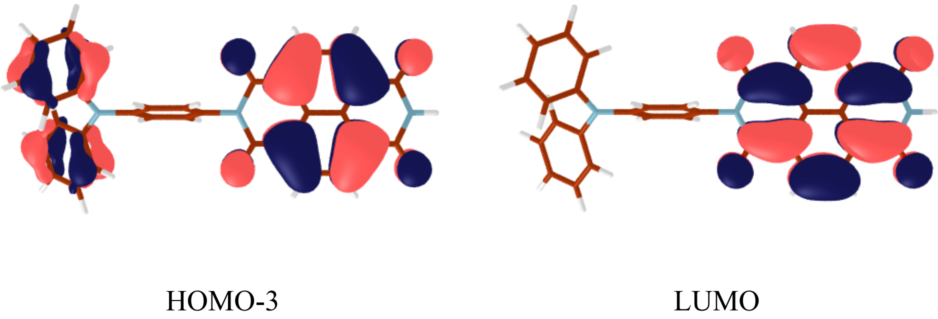


Figure S1. Molecular structure of the NBI-TAA molecule predicted by DFT calculations (B3LYP/6–31G*).



HOMO-3 LUMO

Figure S2. Plots of the molecular orbitals of the NBI-TAA molecule calculated using CAM-B3LYP/6–31G*method.

Table S1. Excitation energies and oscillator strengths for the fifteen lowest singlet-singlet transitions

transition	excitation energy		oscillator strength
	eV	nm	
Singlet-B (HOMO → LUMO)	2.8678	432.32	0.0002
Singlet-A	3.7406	331.45	0.5364
Singlet-B	3.9045	317.54	0.0000
Singlet-B	4.0409	306.83	0.0463
Singlet-B	4.0585	305.49	0.0010
Singlet-A	4.2992	288.39	0.0021
Singlet-A	4.4553	278.29	0.4213
Singlet-B	4.5079	275.03	0.0218
Singlet-A	4.5091	274.96	0.0030
Singlet-A	4.5860	270.35	0.0013
Singlet-B	4.6201	268.36	0.0088
Singlet-B	4.6514	266.55	0.2599
Singlet-A	4.8255	256.94	0.0097
Singlet-B	4.8709	254.54	0.0011
Singlet-B	5.0134	247.31	0.0132

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