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The synthesis and spectral properties of novel 4-phenylacetylene-1,8-naphthalimide derivatives

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Abstract

A series of novel *N*-alkyl-1,8-naphthalimide derivatives with phenylacetylene at the C-4 position were synthesized using 4-bromo-1,8-naphthalimides and arylacetylenes as starting materials in the presence of $Pd(PPh_3)_2Cl_2$/CuI under mild conditions. The absorption and fluorescence properties of these compounds were recorded and the quantum yields were measured in DMF solution using quinine sulphate as the standard. It was found that UV/vis absorption was in the range of 372–399 nm and fluorescence emission was between 428 and 531 nm. Substituent effects on absorption and fluorescence spectra are discussed.

Keywords: 1,8-Naphthalimide; Arylacetylene; Fluorescence quantum yield; Palladium/copper catalysts

1. Introduction

1,8-Naphthalimide derivatives are luminophore compounds that are widely used in various fields of science and technology that exhibit all the necessary optical characteristics for polymer materials and are readily available from a synthetic point of view [1–4]. They have been used as fluorescent brightening agents [5–8] and fluorescent dyes [9,10]. Furthermore, in recent years many organic luminophores with highly π-conjugated systems on phenylacetylene-based moieties have been developed remarkably quickly [11]. The elongated electronic pathways along π-extended conjugations in these molecules often present a bathochromic shift in the absorption and fluorescence spectra [12]. Because of their intriguing electro-conductive, magnetic and optical properties, these compounds can be used as electrical conductors in LED displays [13], fluorescence sensors [14], lasers [15], etc. We report here the synthesis and properties of some novel 1,8-naphthalimide derivatives to which phenylacetylene was conjugated at the 4-position of the naphthalene ring. Synthesis of the compounds was catalyzed using a palladium/copper (Pd/Cu) system and their UV/vis absorption and fluorescence emission spectral properties were studied using prepared solutions in DMF. The respective quantum yields were determined using quinine sulphate as the emission standard.

2. Results and discussion

2.1. Synthesis of 4-phenylacetylene-N-alkyl-1,8-naphthalimides

4-Phenylacetylene-*N*-alkyl-1,8-naphthalimides **3** were synthesized by palladium(0)-catalyzed Sonogashira

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coupling reactions [16] with 4-bromo-1,8-naphthalimides and (un)substituted benzeneacetylenes as starting materials, as shown in Scheme 1.

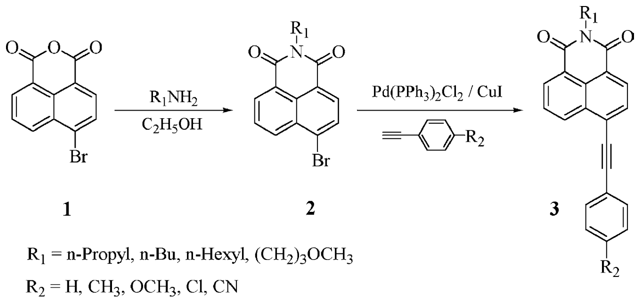
Reactions were carried out using 5 mol% bis-[triphenylphosphine]palladium dichloride as catalyst and 5 mol% CuI as co-catalyst in ethanol at reflux temperature with triethylamine as base. *N*-alkyl-4-bromo-1,8-naphthalimides **2** were conveniently prepared by the condensation of **1** and primary alkylamine in ethanol in good yields. The isolated yields and melting points of products **3** are shown in Table 1.

The yields of compounds **3**, with a 1:1 mole ratio of 4-bromo-1,8-naphthalimides **2** and benzeneacetylenes, were good to excellent in Pd(0)-catalyzed coupling reactions. It was found that changing R_1 or R_2 had little influence on yields, as shown in Table 1, but yields were highest when there was a cyano at the benzeneacetylene (**3f** and **3k**, entries 6 and 11). Compounds with no substituent at the benzeneacetylene had higher yields than those with a methyl at the *p*-position of the benzeneacetylene (**3b**, **3c**, entries 2 and 3; **3g**, **3h**, entries 7 and 8; **3l**, **3m**, entries 12 and 13).

The melting points of compounds **3** ranged from 120 °C to 230 °C. Those of **3b**–**3f** (entries 2–6), which all had an *n*-butyl at the N-position, were higher than those of **3g**–**3k** (entries 7–11), which had an *n*-hexyl at the same position. The melting points of **3a**, **3b**, **3g** and **3l** (entries 1, 2, 7 and 12), which all had a phenylacetylene at the C-4 position of 1,8-naphthalimide, were lower when the N-position carbon chain was extended. The same pattern held for compounds **3c**, **3h**, **3m** (entries 3, 8 and 13), which had a 4-methylphenylacetylene at the C-4 position. In addition, melting points were highest when there was a cyano group at the *p*-position of the phenylacetylene (**3f** and **3k**, entries 6 and 11).

2.2. *UV/vis and fluorescence spectral properties*

The UV/vis absorption and fluorescence spectra of compounds **3** in DMF solution are presented in Table 2. For compounds **3a**, **3b**, **3g** and **3l** (entries 1, 2, 7 and 12), which were unsubstituted at the *p*-position on the phenylacetylene, the maximum absorption ($\lambda_{max,uv}$) was in the range of 374–375 nm, but with a methyl at the *p*-position on the phenylacetylene (**3c**, **3h** and **3m**, entries 3, 8 and 13), the $\lambda_{max,uv}$ was in the range of 378–380 nm. Furthermore, the $\lambda_{max,uv}$ was greatest, 399 nm, when there was a methoxy at the *p*-position of the phenylacetylene (**3d** and **3i**, entries 4 and 9). In contrast, with a chlorine (**3e** and **3j**, entries 5 and 10) or a cyano group (**3f** and **3k**, entries 6 and 11) at the *p*-position of the phenylacetylene, the $\lambda_{max,uv}$ was shifted to 374 nm and 372 nm, respectively. From this it can be seen that the substituents at the *p*-position on the phenylacetylene influenced spectral properties of the 1,8-naphthalimide molecules and that the largest hypsochromic shift in $\lambda_{max,uv}$ occurred when there was a methoxy group at the R_2 position.



Scheme 1. Synthesis of 4-arylacetylene-*N*-alkyl-1,8-napthalimides.

Compounds **3d** and **3i** (entries 4 and 9) have a yellow fluorescence, with maximum emission ($\lambda_{max,fl}$) at 531–533 nm and a great Stock's shift (134 nm), but compounds **3f** and **3k** (entries 6 and 11) have an intense blue-purple fluorescence with a $\lambda_{max,fl}$ at 428 nm, which produced a smaller Stock's shift (56 nm). For the other compounds, the $\lambda_{max,fl}$ was at 446–450 nm, giving an intense blue fluorescence and making them suitable for use as fluorescent brighteners. Apparently, increasing the charge density of the substituents causes the bathothromic shift in the fluorescence emission peak.

The quantum fluorescence yield Φ was determined using absorption and fluorescence spectra of compounds **3** in DMF at a concentration of 1×10^{-6} mol/l. Quinine sulphate, which has a quantum yield of 0.55, was used as the standard [17,18]. From the tabulated data (Table 2), it can be seen that these compounds have quantum yields Φ between 0.25 and 0.75. It should be noted that

Table 1
Synthesis of 4-phenylacetylene-1,8-naphthalimides via palladium-catalyzed coupling of substituted phenylacetylenes with various 4-bromo-1,8-naphthalimides **3**[a]

Entry	Compounds	R_1	R_2	Yield (%)[b]	Mp (°C)
1	**3a**	*n*-Pr	H	81.8	166.5–167.5
2	**3b**	*n*-Bu	H	95.6	146.0–147.0
3	**3c**	*n*-Bu	CH_3	83.8	170.0–171.0
4	**3d**	*n*-Bu	OCH_3	96.6	156.0–157.0
5	**3e**	*n*-Bu	Cl	95.5	160.0–161.0
6	**3f**	*n*-Bu	CN	95.8	228.0–229.0
7	**3g**	*n*-Hex	H	91.8	121.5–123.0
8	**3h**	*n*-Hex	CH_3	86.5	133.0–134.0
9	**3i**	*n*-Hex	OCH_3	91.1	134.0–134.5
10	**3j**	*n*-Hex	Cl	81.9	142.0–142.5
11	**3k**	*n*-Hex	CN	96.2	193.0–194.5
12	**3l**	$(CH_2)_3OCH_3$	H	94.7	140.5–141.0
13	**3m**	$(CH_2)_3OCH_3$	CH_3	92.6	139.5–140.5

[a] Reactions were carried out with **2** (0.40 mmol), alkynes (0.40 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 mmol, 5 mol%), PPh_3 (0.02 mmol, 5 mol%), CuI (0.02 mmol, 5 mol%), ethanol (6 ml) and triethylamine (2 ml) under nitrogen at 70–80 °C for 2 h.

[b] Separated by silica gel column chromatography eluting with a 90:10 hexane:ethyl acetate mixture and recrystallized in ethanol.

Table 2
The UV/vis absorption and fluorescence spectra of compounds **3**

Entry	Compounds	$\lambda_{max,uv}$ (nm)[a]	ε ($\times 10^4$)	$\lambda_{max,fl}$ (nm)[a]	λ (nm)	Φ_F[b]
1	**3a**	374	2.641	447	73	0.70
2	**3b**	374	2.610	446	72	0.71
3	**3c**	380	2.601	462	82	0.75
4	**3d**	399	2.516	531	132	0.27
5	**3e**	374	2.725	446	72	0.72
6	**3f**	372	2.963	428	56	0.25
7	**3g**	375	2.529	446	71	0.70
8	**3h**	379	2.603	462	83	0.69
9	**3i**	399	2.490	533	134	0.37
10	**3j**	374	2.690	450	76	0.65
11	**3k**	372	2.966	428	56	0.25
12	**3l**	374	2.451	450	76	0.65
13	**3m**	378	2.580	462	84	0.67

[a] Selected excitation wavelength of the standard and tested sample was at 350 nm.

[b] Φ was determined by using 1×10^{-6} mol/l quinine sulphate in 0.05 mol/l H_2SO_4 ($\Phi = 0.55$) as the standard.

in compounds with H, CH_3 or Cl present on the phenylacetylene, the quantum yields were in the range of 0.65–0.75 (entries 1–3, 5, 7–8, 10 and 12–13), but when an electron-acceptor cyano substituent (CN–) (entries 6 and 11) or strong electron-donating methoxy group (–OCH_3) (entries 4 and 9) was present on the phenylacetylene of the naphthalimide molecule, the quantum yields decreased dramatically.

3. Conclusions

The maximum UV/vis absorption of 4-phenylacetylene-*N*-alkyl-1,8-naphthalimides prepared in high yields using a palladium catalyst was between 372 and 399 nm and their maximum fluorescence emissions were at 428–533 nm. The fluorescence quantum yields were found to be from 0.25 to 0.75 and the Stoke's shifts were found from 56 to 134 nm. Electron-donating groups have a bathochromic effect on the absorption and fluorescence spectra, while electron-withdrawing groups have a hypsochromic effect on the spectra. Work on further applications is currently underway in our laboratory.

4. Experimental

4.1. Materials and equipment

The spectra of ^{1}H NMR and ^{13}C NMR were recorded on a Mercury Vx 300 (Varian) with TMS as the internal standard. A Nicolet Impact 400 was used to determine the IR spectra. The mass spectra were obtained on an APEXII-FTMS. UV/vis absorption spectra were taken on an HP8452A spectrometer. Fluorescence spectra were recorded using a Perkin–Elmer LS-50B fluorescence spectrophotometer. Silica gel (100–140 mesh) was used for column chromatography. Both ethanol and triethylamine were dried over 4A sieves and distilled. Elemental analyses were recorded on an Elementar Varioel apparatus.

4.2. General procedure for the preparation of substituted 4-benzofuranyl-1,8-naphthalimide

A 25-ml round-bottomed, two-necked flask was charged with 4-bromo-1,8-naphthalimide (135 mg, 0.40 mmol), substituted phenylacetylene (0.40 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 mmol, 14 mg, 5 mol%), PPh_3 (5 mg, 0.02 mmol) and CuI (4 mg, 0.02 mmol). A rubber serum cap was placed over one neck of the flask and a stopcock adapter in the other. The flask was evacuated and filled with nitrogen several times. Dry ethanol (6 ml) and triethylamine (2 ml) were added via syringe through the serum cap. The reaction mixture was then placed in an oil bath at reflux temperature and stirred magnetically under nitrogen for 2 h.

After completion of the reaction, the mixture was cooled to room temperature and was neutralized with diluted hydrochloric acid, then extracted with 20 ml dichloromethane, washed first with 20 ml saturated brine, then twice with distilled water, and dried over $MgSO_4$. After removal of the solvents, products were separated by flash column chromatography on silica gel eluting with a 90:10 hexane:ethyl acetate mixture and then recrystallized in 10 ml ethanol.

*4.2.1. N-Propyl-4-benzeneacetylene-1,8-naphthalimide (**3a**)*

Mp 166.5–167.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (t, $J = 7.5$ Hz, 3H, CH_3), 1.77 (m, $J = 7.5$ Hz, 2H, CH_2), 4.15 ($J = 7.5$ Hz, 2H, CH_2), 7.44 (m, 3H, Ar), 7.67 (m, 2H, Ar), 7.83 (t, $J = 8.4$ Hz, 1H, Ar), 7.94 (d, $J = 7.5$ Hz, 1H, Ar), 8.54 (d, $J = 7.5$ Hz), 8.64 (dd, $J = 7.5$ Hz, 1.2 Hz, 1H, Ar), 8.73 (dd, $J = 8.4$ Hz, 1.2 Hz, 1H, Ar); ^{13}C NMR (300 MHz, $CDCl_3$) δ 11.5, 21.4, 42.0, 86.3, 99.0, 122.1, 122.2, 123.0, 127.4, 127.5, 128.1, 128.6, 129.4, 130.3, 130.7, 131.5, 131.6, 131.9, 132.3, 163.7, 164.0; IR (KBr) ν 3080, 2960, 2940, 2860, 2210, 1700, 1660, 1590, 1360, 1240, 1090, 790, 760 cm^{-1}; Anal. Calcd for $C_{23}H_{17}NO_2$: C, 81.40; H, 5.05; N, 4.13. Found: C, 81.41; H, 5.01; N, 3.93.

*4.2.2. N-Butyl-4-benzeneacetylene-1,8-naphthalimide (**3b**)*

Mp 146.0–147.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, $J = 7.5$ Hz, 3H, CH_3), 1.45 (m, $J = 7.5$ Hz, 2H, CH_2), 1.71 (m, $J = 7.8$ Hz, 2H, CH_2), 4.17 (t, $J = 7.5$ Hz, 2H, CH_2), 7.42 (m, 3H, Ar), 7.66 (m, 2H, Ar), 7.80 (dd, $J = 8.4$ Hz, 7.2 Hz, 1H, Ar), 7.91 (d, $J = 7.5$ Hz, 1H, Ar), 8.51 (d, $J = 7.5$ Hz), 8.60 (dd, $J = 7.5$ Hz, 1.2 Hz, 1H, Ar), 8.68 (dd, $J = 8.4$ Hz, 1.2 Hz, 1H, Ar); ^{13}C NMR (300 MHz, $CDCl_3$) δ 13.8, 20.4, 30.2, 40.3, 86.2, 99.0, 122.1, 122.2, 122.9, 127.3, 127.4, 128.0, 128.6, 129.4, 130.3, 130.6, 131.4, 131.5, 131.9, 132.2, 163.6, 163.9; IR (KBr) ν 3060, 3020, 2940, 2920, 2860, 2200, 1690, 1660, 1580, 1510, 1380, 1350, 1230, 790 760, 690 cm^{-1}; Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.70; H, 5.35; N, 3.72.

4.2.3. *N-Butyl-4-(4-methylbenzeneacetylene)-1,8-naphthalimide (**3c**)*

Mp 170.0–171.0 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.99 (t, $J = 7.5$ Hz, 3H, CH$_3$), 1.47 (m, $J = 7.5$ Hz, 2H, CH$_2$), 1.72 (m, $J = 7.5$ Hz, 2H, CH$_2$), 2.43 (s, 3H, CH$_3$), 4.19 (t, $J = 7.5$ Hz, 2H, CH$_2$), 7.25 (d, $J = 8.4$ Hz, 2H, Ar), 7.57 (d, $J = 8.4$ Hz, 2H, Ar), 7.83 (t, $J = 7.5$ Hz, 1H, Ar), 7.93 (d, $J = 7.8$ Hz, 1H, Ar), 8.73 (dd, $J = 7.5$ Hz, 0.9 Hz, 1H, Ar), 8.54 (d, $J = 7.8$ Hz, 1H, Ar), 8.64 (dd, $J = 7.5$ Hz, 0.9 Hz, 1H, Ar); ^{13}C NMR (300 MHz, CDCl$_3$) δ 13.8, 20.4, 21.6, 30.2, 40.3, 85.8, 99.4, 119.2, 121.9, 123.0, 127.3, 127.8, 128.1, 129.4, 130.4, 130.6, 131.5, 131.6, 131.8, 132.4, 139.8, 163.8, 164.0; IR (KBr) ν 3060, 3020, 2960, 2920, 2860, 2200, 1690, 1660, 1590, 1510, 1380, 1350, 1230, 790 cm^{-1}; Anal. Calcd for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81. Found: C, 81.70; H, 5.85; N, 3.52.

4.2.4. *N-Butyl-4-(4-methoxybenzeneacetylene)-1,8-naphthalimide (**3d**)*

Mp 156.0–157.0 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.99 (t, $J = 7.5$ Hz, 3H, CH$_3$), 1.46 (m, $J = 7.5$ Hz, 2H, CH$_2$), 1.72 (m, 2H, CH$_2$), 3.88 (s, 3H, CH$_3$), 4.19 (t, $J = 7.5$ Hz, 2H, CH$_2$), 6.96 (m, $J = 9.0$ Hz, 2H, Ar), 7.62 (m, $J = 9.0$ Hz, 2H, Ar), 7.82 (dd, $J = 8.4$ Hz, 7.5 Hz, 1H, Ar), 7.92 (d, $J = 7.8$ Hz, 1H, Ar), 8.54 (d, $J = 7.8$ Hz, 1H, Ar), 8.63 (dd, $J = 7.5$ Hz, 1.2 Hz, 1H, Ar), 8.73 (dd, $J = 8.4$ Hz, 1.2 Hz, 1H, Ar); ^{13}C NMR (300 MHz, CDCl$_3$) δ 13.8, 20.4, 30.2, 40.3, 55.4, 85.4, 99.5, 114.3, 121.7, 123.0, 127.3, 128.0, 128.1, 130.4, 131.5, 131.6, 132.4, 133.5, 160.5, 163.8, 164.1; IR (KBr) ν 3010, 2960, 2940, 2860, 2200, 1690, 1660, 1580, 1510, 1380, 1360, 1250, 1180, 1020, 830, 780 cm^{-1}; Anal. Calcd for $C_{25}H_{21}NO_3$: C, 78.31; H, 5.52; N, 3.65. Found: C, 78.43; H, 5.50; N, 3.37.

4.2.5. *N-Butyl-4-(4-chlorobenzeneacetylene)-1,8-naphthalimide (**3e**)*

Mp 160.0–161.0 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.98 (t, $J = 7.2$ Hz, 3H, CH$_3$), 1.45 (m, $J = 7.2$, 2H, CH$_2$), 1.73 (m, $J = 7.5$ Hz, 2H, CH$_2$), 4.17 (t, $J = 7.5$ Hz, 2H, CH$_2$), 7.41 (d, $J = 8.4$ Hz, 2H, Ar), 7.59 (d, $J = 8.4$ Hz, 2H, Ar), 7.82 (dd, $J = 8.4$ Hz, 7.2H, 1H, Ar), 7.92 (d, $J = 7.8$ Hz, 1H, Ar), 8.53 (d, $J = 7.8$ Hz, 1H, Ar), 8.62 (dd, $J = 7.5$ Hz, 1.2 Hz, 1H, Ar), 8.66 (dd, $J = 8.4$ Hz, 1.2 Hz, 1H, Ar); ^{13}C NMR (300 MHz, CDCl$_3$) δ 13.8, 20.4, 30.2, 40.4, 87.2, 97.7, 12.7, 122.4, 123.1, 127.1, 127.5, 128.1, 129.0, 130.3, 130.8, 131.5, 131.6, 132.2, 133.1, 135.6, 163.7, 164.0. IR (KBr) ν 3100, 3080, 2960, 2940, 2860, 2210, 1690, 1660, 1590, 1380, 1350, 1230, 1090, 840, 780, 750 cm^{-1}; Anal. Calcd for $C_{24}H_{18}ClNO_2$: C, 74.32; H, 4.68; N, 3.61. Found: C, 74.30; H, 4.64; N, 3.36.

4.2.6. *N-Butyl-4-(4-cyanobenzeneacetylene)-1,8-naphthalimide (**3f**)*

Mp 228.0–229.0 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.99 (t, $J = 7.5$ Hz, 3H, CH$_3$), 1.46 (m, $J = 7.8$ Hz, 2H, CH$_2$), 1.72 (m, $J = 7.5$ Hz, 2H, CH$_2$), 4.19 (t, $J = 7.5$ Hz, 2H, CH$_2$), 7.43 (d, $J = 8.7$ Hz, 2H, Ar), 7.80 (d, $J = 8.7$ Hz, 2H, Ar), 7.87 (t, $J = 7.5$ Hz, 1H, Ar), 7.99 (d, $J = 7.8$ Hz, 1H, Ar), 8.58 (d, $J = 7.8$ Hz, 1H, Ar), 8.67 (d, $J = 7.5$ Hz, 1H, Ar), 8.68 (d, $J = 8.4$ Hz, 1H, Ar); IR (KBr) ν 3100, 3080, 2960, 2940, 2860, 2210, 1700, 1660, 1580, 1380, 1350, 1230, 1090, 840, 780 cm^{-1}; HRMS (M$^+$): Calcd for $C_{25}H_{18}N_2O_2$: 378.1368. Found: 378.1361.

4.2.7. *N-Hexyl-4-benzeneacetylene-1,8-naphthalimide (**3g**)*

Mp 121.5–123.0 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.89 (t, $J = 7.5$ Hz, 3H, CH$_3$), 1.38 (m, 6H, 3CH$_2$), 1.73 (m, $J = 7.5$ Hz, 2H, CH$_2$), 4.16 (t, $J = 7.8$ Hz, 2H, CH$_2$), 7.44 (m, 3H, Ar), 7.66 (m, 2H, Ar), 7.81 (t, $J = 8.1$ Hz, 1H, Ar), 7.93 (d, $J = 7.8$ Hz, 1H, Ar), 8.53 (d, $J = 7.8$ Hz, 1H, Ar), 8.62 (dd, $J = 7.5$ Hz, 1.2 Hz, 1H, Ar), 8.70 (d, $J = 8.4$ Hz, 1H, Ar); ^{13}C NMR (300 MHz, CDCl$_3$) IR (KBr) ν 2960, 2940, 2920, 2860, 2200, 1690, 1660, 1580, 1380, 1360, 1240, 780, 760 cm^{-1}; Anal. Calcd for $C_{26}H_{23}NO_2$: C, 81.86; H, 6.08; N, 3.67. Found: C, 81.87; H, 6.14; N, 3.47.

4.2.8. *N-Hexyl-4-(4-methylbenzeneacetylene)-1,8-naphthalimide (**3h**)*

Mp 133.0–134.0 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.89 (t, $J = 6.9$ Hz, 3H, CH$_3$), 1.40 (m, 6H, 3CH$_2$), 1.73 (m, $J = 7.8$ Hz, 2H, CH$_2$), 2.42 (s, 3H, CH$_3$), 4.16 (t, $J = 7.5$ Hz, 1H, CH$_2$), 7.24 (d, $J = 8.4$ Hz, 2H, Ar), 7.56 (d, $J = 8.4$ Hz, 2H, Ar), 7.81 (t, $J = 7.8$ Hz, 1H, Ar), 7.91 (d, $J = 7.8$ Hz, 1H, Ar), 8.52 (d, $J = 7.5$ Hz, 1H, Ar), 8.61 (dd, $J = 7.2$ Hz, 0.6 Hz, 1H, Ar), 8.70 (dd, $J = 8.4$ Hz, 0.6 Hz, 1H, Ar); ^{13}C NMR (300 MHz, CDCl$_3$) δ 14.0, 21.6, 22.5, 26.8, 28.0, 31.5, 40.5, 85.8, 99.4, 119.2, 121.9, 123.0, 127.3, 127.8, 128.0, 129.4, 130.3, 130.5, 131.5, 131.8, 132.3, 139.8, 163.7, 164.0; IR (KBr) ν 3020, 2980, 2940, 2860, 2200, 1690, 1660, 1580, 1380, 1360, 1240, 1090, 820, 780 cm^{-1}; Anal. Calcd for $C_{27}H_{25}NO_2$: C, 82.00; H, 6.37; N, 3.54. Found: C, 81.92; H, 6.34; N, 3.34.

4.2.9. *N-Hexyl-4-(4-methoxybenzeneacetylene)-1,8-naphthalimide (**3i**)*

Mp 134.0–134.5 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.89 (t, $J = 6.9$ Hz, 3H, CH$_3$), 1.40 (m, 6H, 3CH$_2$), 1.71 (m, 2H, $J = 7.2$ Hz, CH_2), 3.88 (s, 3H, CH_3), 4.17 (t, $J = 7.5$ Hz, 2H, CH_2), 6.96 (m, $J = 8.7$ Hz, 2H, Ar), 7.62 (m, $J = 9.0$ Hz, 2H, Ar), 7.82 (dd, $J = 8.4$ Hz, 7.5 Hz, 1H, Ar), 7.91 (d, $J = 7.5$ Hz, 1H, Ar), 8.54 (d, $J = 7.8$ Hz, 1H, Ar), 8.63 (dd, $J = 7.5$ Hz, 1.2 Hz, 1H, Ar), 8.74 (dd, $J = 8.4$ Hz, 1.2 Hz, 1H, Ar); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.0, 22.6, 26.8, 28.1, 31.5, 40.5, 55.4, 85.4, 99.5, 114.3, 121.8, 123.0, 127.3, 128.0, 130.3, 130.4, 131.5, 131.6, 128.1, 132.4, 133.5, 160.6, 163.8, 164.0; IR (KBr) ν 3080, 3040, 2960, 2940, 2860, 2200, 1690, 1660, 1580, 1510, 1380, 1360, 1250, 1180, 830, 790 cm^{-1}; Anal. Calcd for $C_{27}H_{25}NO_3$: C, 78.81; H, 6.12; N, 3.40. Found: C, 78.65; H, 6.01; N, 3.22.

4.2.10. *N-Hexyl-4-(4-chlorobenzeneacetylene)-1,8-naphthalimide (**3j**)*

Mp 142.0–142.5 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, $J = 6.9$ Hz, 3H, CH_3), 1.45 (m, 6H, $3CH_2$), 1.75 (m, 2H, $J = 7.2$ Hz, CH_2), 4.19 (t, $J = 7.8$ Hz, 2H, CH_2), 7.44 (m, $J = 9.0$ Hz, 2H, Ar), 7.63 (m, $J = 8.4$ Hz, 2H, Ar), 7.86 (dd, $J = 8.4$ Hz, 7.5 Hz, 1H, Ar), 7.96 (d, $J = 7.5$ Hz, 1H, Ar), 8.57 (d, $J = 7.8$ Hz, 1H, Ar), 8.66 (dd, $J = 7.5$ Hz, 1.2 Hz, 1H, Ar), 8.71 (dd, $J = 8.4$ Hz, 0.6 Hz, 1H, Ar); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.0, 22.6, 26.8, 28.1, 31.5, 40.6, 87.2, 97.7, 120.7, 122.4, 123.1, 127.1, 127.5, 128.1, 129.0, 130.3, 130.8, 131.5, 131.6, 132.1, 133.1, 135.6, 163.7, 163.9; IR (KBr) ν 3060, 2970, 2950, 2860, 2200, 1700, 1660, 1590, 1390, 1360, 1240, 1090, 830, 780 cm^{-1}; Anal. Calcd for $C_{26}H_{22}ClNO_2$: C, 75.08; H, 5.33; N, 3.37. Found: C, 74.95; H, 5.41; N, 3.20.

4.2.11. *N-Hexyl-4-(4-cyanobenzeneacetylene)-1,8-naphthalimide (**3k**)*

Mp 193.0–194.5 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, $J = 6.9$ Hz, 3H, CH_3), 1.38 (m, 6H, $3CH_2$), 1.71 (m, $J = 7.5$ Hz, 2H, CH_2), 4.17 (t, $J = 7.8$ Hz, 2H, CH_2) 7.73 (d, $J = 8.7$ Hz, 2H, Ar), 7.78 (d, $J = 8.7$ Hz, 2H, Ar), 7.86 (t, $J = 7.8$ Hz, 1H, Ar), 7.98 (d, $J = 7.5$ Hz, 1H, Ar), 8.57 (d, $J = 7.5$ Hz, 1H, Ar), 8.66 (d, $J = 7.2$ Hz, 1H, Ar), 8.67 (d, $J = 8.7$ Hz, 1H, Ar); ^{13}C NMR (300 MHz, $CDCl_3$) IR (KBr) ν 3100, 3080, 2960, 2920, 2860, 2210, 1700, 1660, 1590, 1380, 1360, 1240, 1090, 840, 780 cm^{-1}; HRMS (M^+): Calcd for $C_{27}H_{22}N_2O_2$: 406.1681. Found: 406.1667.

4.2.12. *N-(3-Methoxypropyl)-4-benzeneacetylene-1,8-naphthalimide (**3l**)*

Mp 140.5–141.0; ^1H NMR (300 MHz, $CDCl_3$) δ 2.04 (t, $J = 7.5$ Hz, 3H, CH_3), 3.34 (s, 3H, CH_3), 3.53 (t, $J = 6.3$ Hz, 2H, CH_2), 4.29 (t, $J = 7.2$ Hz, 2H, CH_2), 7.45 (t, 3H, Ar), 7.68 (m, 2H, Ar), 7.84 (t, $J = 7.8$ Hz, 1H, Ar), 7.95 (d, $J = 7.2$ Hz, 1H, Ar), 8.56 (d, $J = 7.8$ Hz, 1H, Ar), 8.64 (dd, $J = 7.2$ Hz, 1.2 Hz, 1H, Ar), 8.74 (dd, $J = 8.4$ Hz, 1.2 Hz, 1H, Ar); ^{13}C NMR (300 MHz, $CDCl_3$) δ 28.2, 38.0, 58.5, 70.6, 86.2, 99.0, 122.1, 122.2, 123.0, 127.4, 127.6, 128.1, 128.6, 129.4, 130.4, 130.7, 131.5, 131.6, 131.9, 132.4, 163.7, 164.0; IR (KBr) ν 3080, 2960, 2940, 2860, 2810, 2200, 1700, 1660, 1580, 1380, 1350, 1230, 1110, 780, 760 cm^{-1}; Anal. Calcd for $C_{24}H_{19}NO_3$: C, 78.03; H, 5.18; N, 3.79. Found: C, 77.96; H, 5.12; N, 3.60.

4.2.13. *N-(3-Methoxypropyl)-4-(4-methylbenzeneacetylene)-1,8-naphthalimide (**3m**)*

Mp 139.5–140.5 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.03 (t, $J = 7.5$ Hz, 3H, CH_3), 2.42 (s, 3H, CH_3), 3.34 (s, 3H, CH_3), 3.53 (t, $J = 6.3$ Hz, 2H, CH_2), 4.29 (t, $J = 7.2$ Hz, 2H, CH_2), 7.24 (d, $J = 7.8$ Hz, 2H, Ar), 7.57 (d, $J = 7.8$ Hz, 2H, Ar), 7.82 (dd, $J = 8.1$ Hz, 7.2 Hz, 1H, Ar), 7.93 (d, $J = 7.5$ Hz, 1H, Ar), 8.54 (d, $J = 7.8$ Hz, 1H, Ar), 8.63 (dd, $J = 7.5$ Hz, 1.2 Hz, 1H, Ar), 8.72 (dd, $J = 8.4$ Hz, 1.2 Hz, 1H, Ar); ^{13}C NMR (300 MHz, $CDCl_3$) δ 21.6, 28.2, 38.0, 58.5, 70.6, 85.8, 99.5, 119.2, 121.9, 123.0, 127.3, 127.9, 128.1, 129.4, 130.4, 130.6, 131.5, 131.6, 131.8, 132.4, 139.8, 163.7, 164.0; IR (KBr) ν 3040, 3020, 2980, 2940, 2860, 2200, 1700, 1660, 1580, 1380, 1360, 1240, 1120, 1070, 820, 780 cm^{-1}; Anal. Calcd for $C_{25}H_{21}NO_3$: C, 78.31; H, 5.52; N, 3.65. Found: C, 78.27; H, 5.56; N, 3.38.

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