Supplementary Information to

Deep in Blue with Green Chemistry: Solvent and Chain Length Influence in the Behaviour of *N*- and *N,N'*- alkyl Indigo Derivatives

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Synthesis of the *N*-alkyl Indigo Derivatives

***N*-methylindigo (NC_1Ind):** Prepared from iodomethane and indigo, and the title compound was isolated as a blue solid (0.220 g, 44% yield). **^{1}H NMR ($CDCl_3$, 400 MHz)**, δ 10.52 (s, 1H), 7.73 (d, *J*=7.6 Hz, 1H), 7.68 (d, *J*=7.8 Hz, 1H), 7.56 (dt, *J*=1.2 Hz, *J*=7.2 Hz, 1H), 7.46 (dt, *J*=1.2 Hz, *J*=7.2 Hz, 1H), 7.07 (d, *J*=8.2 Hz, 1H), 7.04-6.99 (m, 2H), 6.95 (t, *J*=7.4 Hz, 1H), 3.88 (s,3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)**, δ 189.86, 186.95, 153.69, 151.39, 135.98, 135.86, 125.13, 124.70, 124.02, 120.66, 120.38, 111.85, 110.48, 35.31 ppm. **HRMS** (**ESI-TOF-MS):** m/z $[M+1]^+$ = 277.09715 calculated for $C_{17}H_{13}N_2O_2$; found: 277.09708.

***N*-ethylindigo (NC_2Ind):** Prepared from iodoethane and indigo, and the title compound was isolated as a blue solid (0.103 g, 34% yield). **^{1}H NMR ($CDCl_3$, 400 MHz)**, δ 10.78 (s, 1H), 7.74 (d, *J*=7.2 Hz, 1H), 7.68 (d, *J*=7.2 Hz, 1H), 7.54 (t, *J*=7.2 Hz, 1H), 7.46 (t, *J*=7.2 Hz, 1H), 7.10 (d, *J*=8.0 Hz, 1H), 7.02-6.98 (m, 2H), 6.94 (t, *J*=7.2 Hz, 1H), 4.56 (d, *J*=6.7 Hz, 2H), 1.31 (t, *J*=6.5 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)**, δ 190.04, 187.19, 152.29, 151.35, 135.99, 135.83, 125.36, 124.70, 124.21, 120.58, 120.52, 120.24, 111.81, 110.46, 42.11, 13.96 ppm. **GC-MS:** m/z $[M^+]$ = 290.1.

***N*-propylindigo (NC_3Ind):** Prepared from 1-iodopropane and indigo, and the title compound was isolated as a blue solid (0.016 g, 32% yield). **^{1}H NMR ($CDCl_3$, 400 MHz)**, δ 10.83 (s, 1H), 7.73 (d, *J*=7.6 Hz, 1H), 7.68 (d, *J*=7.6 Hz, 1H), 7.53 (dt, *J*=1.2, *J*=7.2 Hz, 1H), 7.46 (t, *J*=1.2, *J*=6.8 Hz, 1H), 7.09 (d, *J*=8.3 Hz, 1H), 7.00 (m, 2H), 6.94 (t, *J*=7.4 Hz, 1H), 4.48 (t, *J*=7.6 Hz, 2H), 1.74 (sex, *J*=7.2 Hz, 2H), 0.96 (t, *J*=7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)**, δ 189.92, 187.16, 152.57, 151.32, 135.95, 135.73, 125.42, 124.72, 124.17, 122.68, 120.55, 120.42, 120.25, 111.80, 110.60, 48.53, 22.16, 11.06 ppm. **HRMS** (**ESI-TOF-MS):** m/z $[M+1]^+$ = 305.12845 calculated for $C_{19}H_{17}N_2O_2$; found: 305.12930.

***N*-hexylindigo (NC_6Ind):** Prepared from 1-iodohexane and indigo, and the title compound was isolated as a blue solid (0.137 g, 46% yield). **^{1}H NMR ($CDCl_3$, 400 MHz)**, δ 10.81 (s, 1H), 7.72 (d, *J*=7.6 Hz, 1H), 7.68 (d, *J*=7.6 Hz, 1H), 7.52 (dt, *J*=1.2 Hz, *J*=7.2 Hz, 1H), 7.45 (dt, *J*=1.2 Hz, *J*=7.2 Hz, 1H), 7.07 (d, *J*=8.3 Hz, 1H), 7.01-6.97, (m,

2H), 6.93 (t, *J*=7.4 Hz, 1H), 4.50 (t, *J*=7.6 Hz, 2H), 1.72-1.64 (m, 2H), 1.30-1.25 (m, 6H), 0.85 (t, *J*=7.0 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)**, δ 189.97, 187.10, 152.55, 151.31, 135.92, 135.74, 125.40, 124.73, 124.16, 122.64, 120.65, 120.54, 120.42, 120.25, 111.80, 110.62, 47.08, 31.62, 28.70, 26.35, 22.59, 13.99 ppm. **GC-MS:** m/z $[M^+]$ = 346.2.

***N*-octylindigo (NC_8Ind):** Prepared from 1-iodooctane and indigo, and the title compound was isolated as a blue solid (0.211 g, 42% yield). **^{1}H NMR ($CDCl_3$, 400 MHz)**, δ 10.81 (s, 1H), 7.73 (d, *J*=7.5 Hz, 1H), 7.68 (d, *J*=7.6 Hz, 1H), 7.53 (dt, *J*=1.2 Hz, *J*=7.2 Hz, 1H), 7.45 (dt, *J*=1.2 Hz, *J*=8.3 Hz, 1H), 7.08 (d, *J*=8.3 Hz, 1H), 7.01 – 6.98 (m, 2H), 6.94 (t, *J*=7.4 Hz, 1H), 4.50 (t, *J*=7.2 Hz, 2H), 1.71-1.63(m, 2H), 1.33-1.23 (m, 10H), 0.85 (t, *J*=6.8 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)**, δ 189.97, 187.09, 152.56, 151.31, 135.92, 135.74, 125.40, 124.74, 124.17, 122.65, 120.66, 120.54, 120.42, 120.26, 111.79, 110.64, 47.06, 31.79, 29.42, 29.22, 28.71, 26.68, 22.62, 14.08 ppm. **HRMS** (**ESI-TOF-MS):** m/z $[M+1]^+$ = 375.20670 calculated for $C_{24}H_{27}N_2O_2$; found: 375.20648.

***N*-dodecylindigo (NC_{12}Ind):** Prepared from 1-iodododecane and indigo, and the title compound was isolated as a blue solid (0.026 g, 52% yield). **^{1}H NMR ($CDCl_3$, 400 MHz)**, δ 10.81 (s, 1H), 7.73 (d, *J*=7.6 Hz, 1H), 7.68 (d, *J*=7.96 Hz, 1H), 7.53 (dt, *J*=1.2 Hz, *J*=7.2 Hz, 1H), 7.46 (dt, *J*=1.2 Hz, *J*=7.2 Hz, 1H), 7.08 (d, *J*=8.3 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.93 (t, *J*=7.4 Hz, 1H), 4.50 (t, *J*=7.6 Hz, 1H), 1.70-1.65 (m, 2H), 1.36-1.26 (m, 18H), 0.87 (t, *J*=6.8 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)**, δ 189.97, 187.09, 152.56, 151.30, 135.92, 135.74, 125.40, 124.73, 124.16, 122.65, 120.66, 120.54, 120.42, 120.25, 111.79, 110.64, 47.06, 31.91, 29.63, 29.61, 29.56, 29.55, 29.45, 29.33, 28.70, 26.66, 22.69, 14.12 ppm. **GC-MS:** m/z $[M^+]$ = 430.4.

***N*-octadecylindigo (NC_{18}Ind):** Prepared from 1-iodooctadecane and indigo, and the title compound was isolated as a blue solid (0.023 g, 46% yield). **^{1}H NMR ($CDCl_3$, 400 MHz)**, δ 10.81 (s, 1H), 7.73 (d, *J*=7.6 Hz, 1H), 7.68 (d, *J*=7.6 Hz, 1H), 7.53 (dt, *J*=1.2 Hz, *J*=7.2 Hz, 1H), 7.45 (dt, *J*=1.2 Hz, *J*=7.2 Hz, 1H), 7.08 (d, *J*=8.3 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.94 (t, *J*=7.4 Hz, 1H), 4.50 (t, *J*=7.6 Hz, 1H), 1.70-1.63 (m, 2H), 1.30-1.25 (m, 30H), 0.88 (t, *J*=6.8 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)**, δ 189.98, 187.10,

152.56, 151.31, 135.92, 135.74, 125.40, 124.74, 124.17, 122.66, 120.66, 120.54, 120.42, 120.26, 111.79, 110.64, 47.07, 31.93, 29.71, 29.71, 29.71, 29.67, 29.67, 29.67, 29.58, 29.56, 29.46, 29.37, 28.71, 26.67, 22.70, 14.13 ppm. **HRMS** (**ESI-TOF-MS):** m/z $[M+1]^+$ = 515.36321 calculated for $C_{34}H_{47}N_2O_2$; found: 515.36479.

Synthesis of the *N,N'*-dialky Indigo Derivatives

***N,N'*-dimethylindigo (N,N'C_1Ind):** Prepared from iodomethane and indigo, and the title compound was isolated as a green solid (0.264 g, 53% yield). **^{1}H NMR (400 MHz, $CDCl_3$)**, δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.54 (dt, *J*=1.2 Hz, *J*=7.2 Hz 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 7.05 (dt, *J*= 0.8 Hz, *J* = 7.2 Hz, 2H), 3.59 (s, 6H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)**, δ 185.29, 153.09, 135.03, 126.28, 123.89, 121.61, 121.21, 110.52, 36.57 ppm. **GC-MS:** m/z $[M^+]$ = 290.1.

***N,N'*-diethylindigo (N,N'C_2Ind):** Prepared from iodoethane and indigo, and the title compound was isolated as a green solid (0.104 g, 35% yield). **^{1}H NMR ($CDCl_3$, 400 MHz)**, δ 7.71 (d, *J*= 7.6 Hz, 2H), 7.52 (dt, *J*=1.2 Hz, *J*=7.2 Hz, 2H), 7.13 (d, *J*= 8.2 Hz, 2H), 7.02 (dt, , *J*= 0.8 Hz, *J*= 7.6 Hz, 2H), 4.25 (q, *J*= 7.2 Hz, 4H), 1.18 (t, *J*= 7.1 Hz, 6H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)**, δ 186.08, 152.24, 134.97, 125.51, 124.14, 122.28, 121.16, 111.27, 42.81, 12.53 ppm. **GC-MS:** m/z $[M^+]$ = 318.1.

***N,N'*-dipropylindigo (N,N'C_3Ind):** Prepared from 1-iodopropane and indigo, and the title compound was isolated as a green solid (0.018 g, 36% yield). **^{1}H NMR ($CDCl_3$, 400 MHz)**, δ 7.71 (d, *J*= 7.4 Hz, 2H), 7.51 (dt, *J*=1.2 Hz, *J*=7.2 Hz, 2H), 7.13 (d, *J*= 8.2 Hz, 2H), 7.01 (dt, *J*=0.8 Hz, *J*= 7.6 Hz, 2H), 4.19 (t, *J*=7.2 Hz, 4H), 1.63 (sex, *J*=7.2 Hz, 4H), 0.82 (t, *J*= 7.4 Hz, 6H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)**, δ 185.76, 152.56, 134.94, 125.74, 124.29, 122.10, 121.17, 111.53, 49.74, 20.51, 11.56 ppm. **GC-MS:** m/z $[M^+]$ = 346.2.

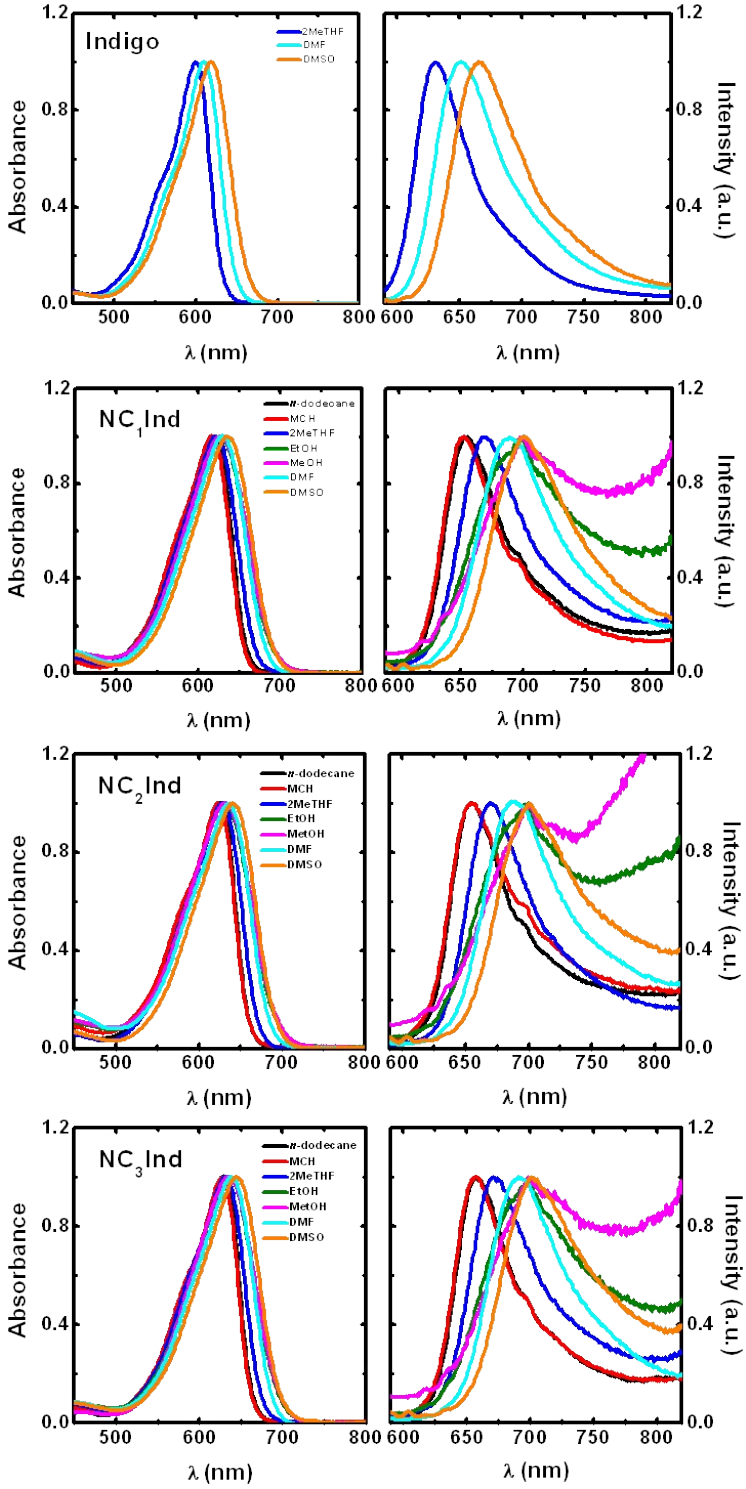
***N,N'*-dihexylindigo (N,N'C_6Ind):** Prepared from 1-iodohexane and indigo, and the title compound was isolated as a green solid (0.157 g, 52% yield). **^{1}H NMR ($CDCl_3$, 400 MHz)**, δ 7.64 (d, *J*=7.0 Hz, 2H), 7.44 (dt, *J*=1.2 Hz, *J*=7.2 Hz, 2H), 7.05 (d, *J*= 8.2 Hz, 2H), 6.95 (dt, *J*=0.8, *J*=7.3 Hz, 2H), 4.15 (t, *J*=7.2 Hz, 4H), 1.51-1.46 (m, 4H), 1.15-1.06

(m, 12H), 0.73 (t, *J*= 6.6 Hz, 6H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)**, δ 185.63, 152.35, 134.79, 125.56, 124.15, 122.04, 121.01, 111.36, 47.94, 31.48, 29.70, 27.08, 26.68, 22.50, 13.91 ppm. **GC-MS:** m/z [M^+] = 430.4.

***N,N'*-dioctylindigo (N,N'C_8Ind):** Prepared from 1-iodooctane and indigo, and the title compound was isolated as a green solid (0.253 g, 51% yield). **^{1}H NMR (400 MHz, $CDCl_3$)**, δ 7.70 (d, *J*=7.5 Hz, 2H), 7.51 (dt, *J*=1.2 Hz, *J*=7.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.01 (dt, *J*=0.8 Hz, *J*=6.8 Hz 2H), 4.23 (t, *J*= 7.4 Hz, 4H), 1.58-1.52 (m, 4H), 1.23-1.11 (m, 20H), 0.82 (t, *J* = 6.6 Hz, 6H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)**, δ 185.62, 152.35, 134.79, 125.55, 124.15, 122.04, 121.00, 111.35, 47.89, 31.74, 29.28, 29.15, 27.08, 27.01, 22.57, 14.03 ppm. **HRMS** (**ESI-TOF-MS):** m/z $[M+1]^+$ = 487.3319 calculated for $C_{32}H_{43}N_2O_2$; found: 487.3317.

***N,N'*-didodecylindigo (N,N'C_{12}Ind):** Prepared from 1-iododododecane and indigo, and the title compound was isolated as a green solid (0.023 g, 47% yield). **^{1}H NMR (400 MHz, $CDCl_3$)**, δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.51 (dt, *J* = 1.2 Hz, *J* = 7.2 Hz 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 2H), 4.22 (t, J=7.6 Hz, 4H), 1.62-1.51 (m, 4H), 1.21-1.14 (m, 40H), 0.86 (t, *J* = 6.9 Hz, 6H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)**, δ 185.62, 152.34, 134.78, 125.55, 124.15, 122.04, 121.00, 111.35, 47.84, 31.90, 29.70, 29.61, 29.56, 29.51, 29.33, 27.07, 27.00, 22.68, 14.11 ppm. **HRMS** (**ESI-TOF-MS):** m/z $[M+1]^+$ = 599.4571 calculated for $C_{40}H_{59}N_2O_2$; found: 599.4577.

***N,N'*-dioctadecylindigo (N,N'C_{18}Ind):** Prepared from 1-iodooctadecane and indigo, and the title compound was isolated as a green solid (0.026 g, 51% yield). **^{1}H NMR (400 MHz, $CDCl_3$)**, δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.50 (dt, *J*=1.2 Hz, *J*=8.4 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 2H), 4.22 (t, *J*=7.2 Hz, 4H), 1.63-1.50 (m, 4H), 1.23-1.13 (m, 60H), 0.88 (t, *J* = 6.8 Hz, 6H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)**, δ 185.61, 152.34, 134.78, 125.55, 124.15, 122.04, 121.00, 111.35, 47.89, 31.93, 29.71, 29.70, 29.67, 29.63, 29.58, 29.52, 29.37, 29.34, 27.07, 27.01, 22.70, 14.12 ppm. **HRMS** (**ESI-TOF-MS):** m/z $[M+1]^+$ = 767.6449 calculated for $C_{52}H_{83}N_2O_2$; found: 767.6441.


Indigo
2MeTHF
DMF
DMSO
NC1Ind
NC2Ind
NC3Ind
n-dodecane
MCH
2MeTHF
EtOH
MeOH
DMF
DMSO
Absorbance
Intensity (a.u.)
λ (nm)

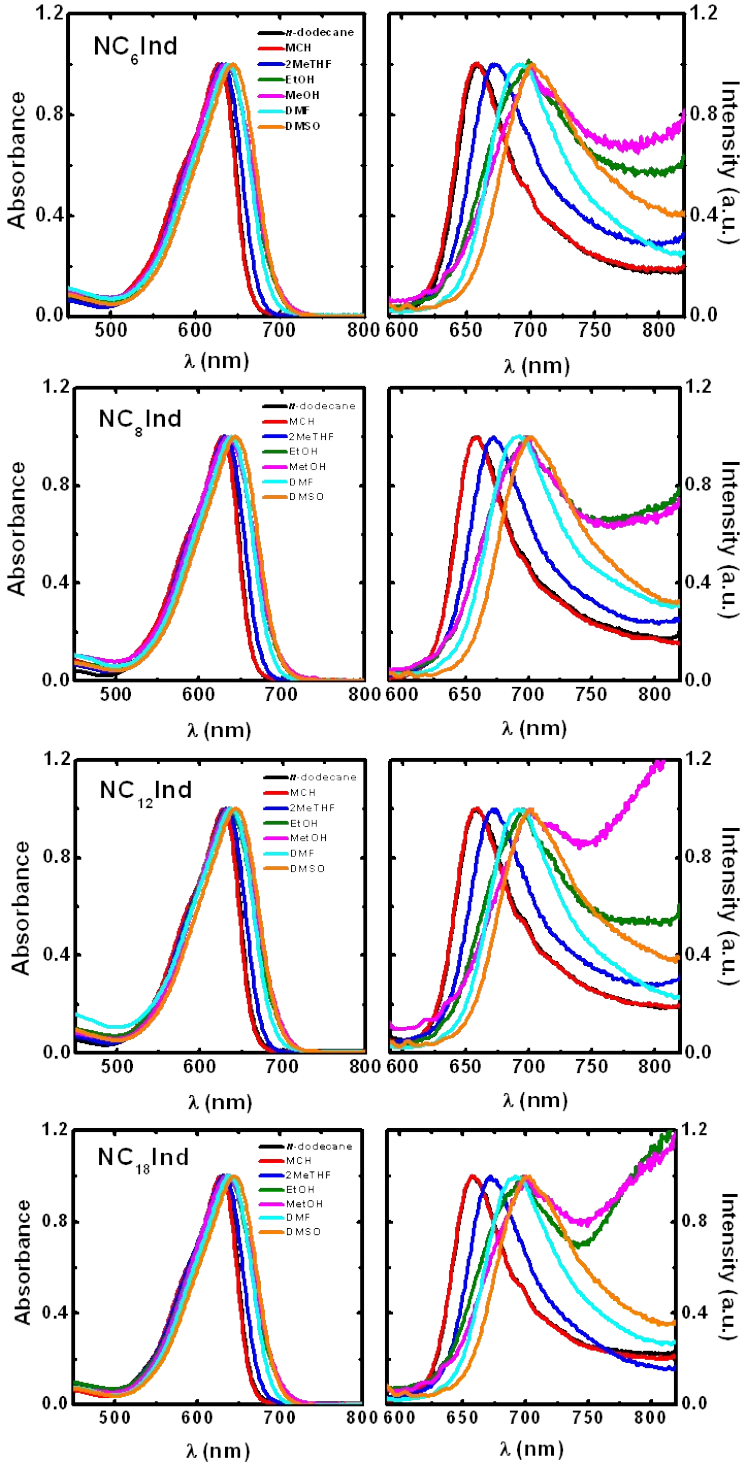
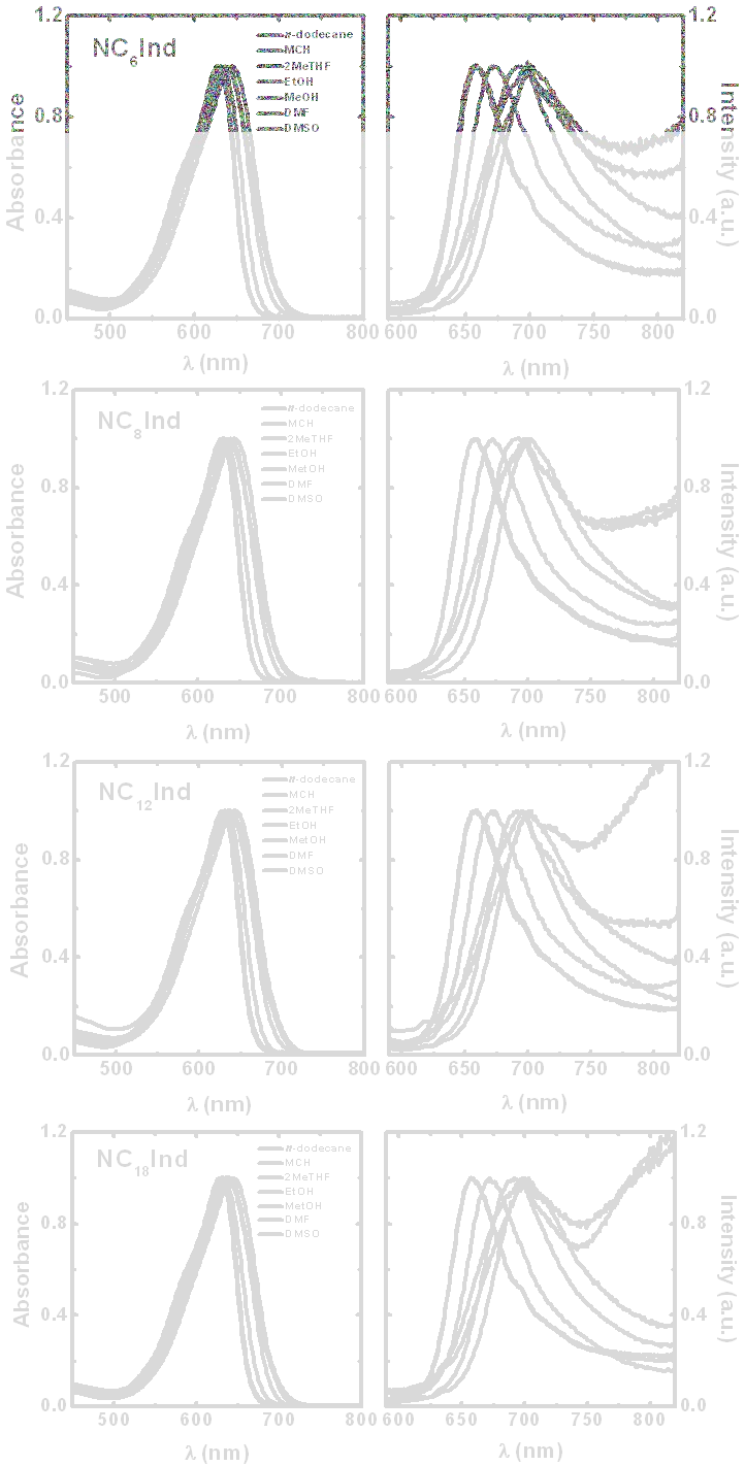


Fig. SI1 Normalized absorption (**left**) and fluorescence emission spectra (λ_{exc}=580nm) (**right**) of *N*-alkyl indigo derivatives in *n*-dodecane, MCH, 2MeTHF, EtOH, MetOH, DMF and DMSO solutions at T = 293 K. For indigo the same parameters are also presented in 2MeTHF, DMF and DMSO for comparison.


NC6Ind
NC8Ind
NC12Ind
NC18Ind
n-dodecane
MCH
2MeTHF
EtOH
MeOH
DMF
DMSO
Absorbance
Intensity (a.u.)
λ (nm)
0.0
0.4
0.8
1.2
500
600
700
800
650
750

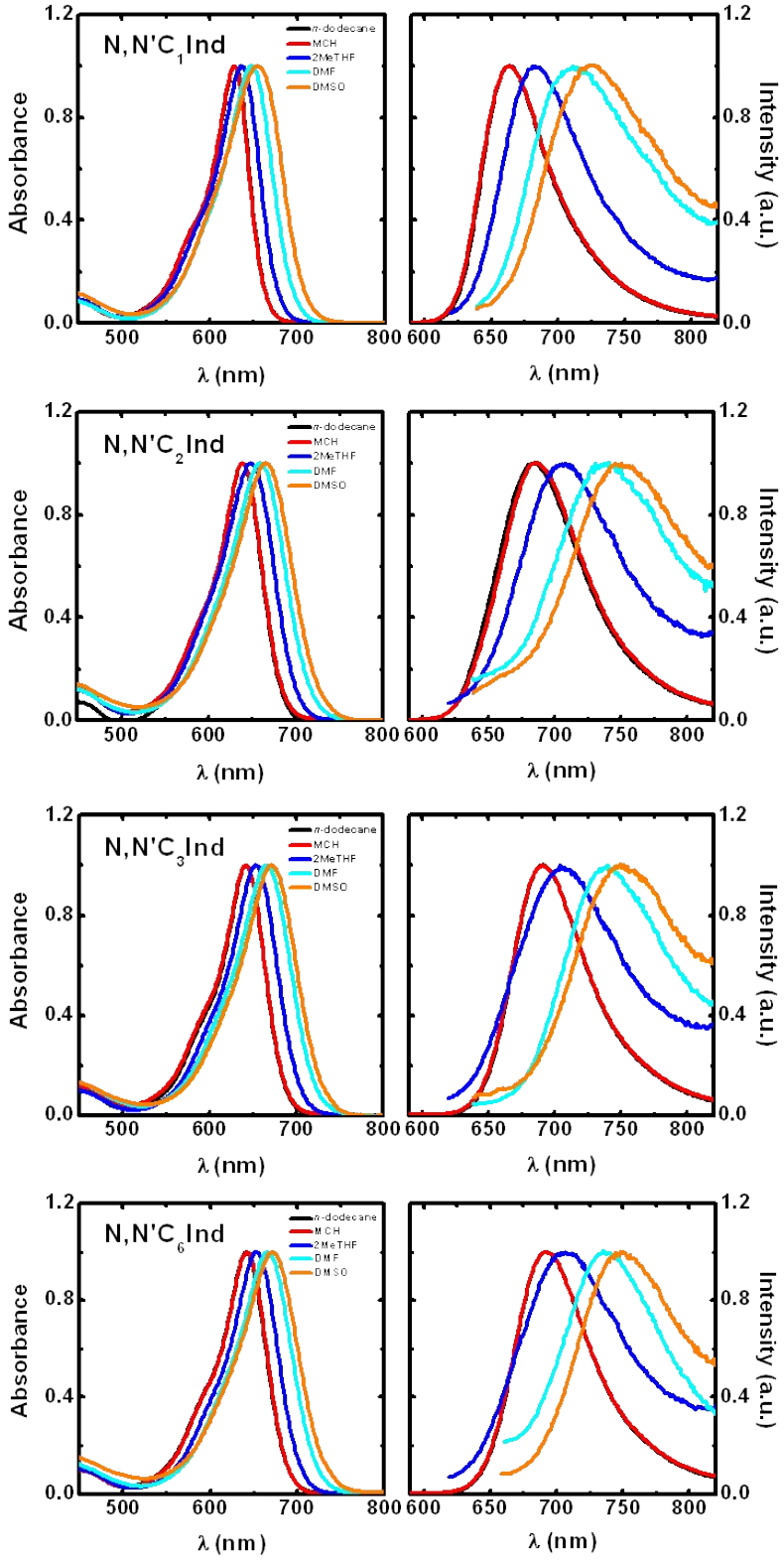
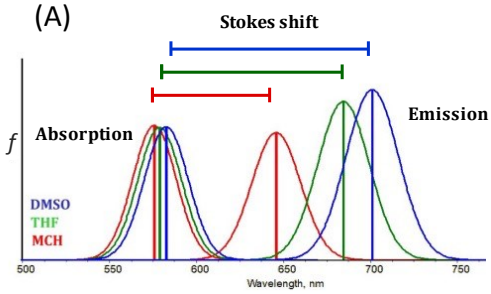


Fig. SI2 Normalized absorption (**left**) and fluorescence emission spectra (**right**) of *N,N'*-dialkyl indigo derivatives in *n*-dodecane, MCH (λ_{exc}=580nm), 2MeTHF (λ_{exc}=610nm), DMF and DMSO (λ_{exc}=630nm) solutions at T = 293 K.

Table SI1 - Dipole moments of the ground state and excited singlet state for the adiabatically relaxed and relaxed with S_1 geometry structures at absorption and emission geometry for NC_1Ind in MCH, DMSO and THF.

NC_1Ind	Absorption S_o/S_1 (D)	Emission S_o/S_1 (D)
MCH	1.2/1.1	1.7/0.9
DMSO	1.5/1.5	2.0/1.8
THF	1.4/1.5	1.9/1.5
$\Delta_{MCH-DMSO}$	0.3/0.4 (25%/36%)	0.3/0.9 (18%/100%)

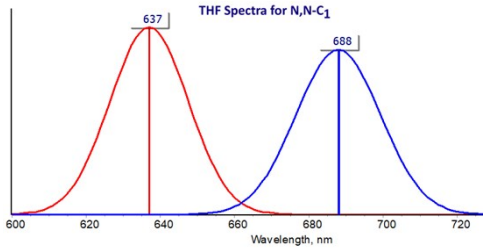
(A)



(B)

eV	Excitation energy	Emission Energy
MCH	2.153	1.919
THF	2.141	1.811
DMSO	2.129	1.769

(C)



(D)

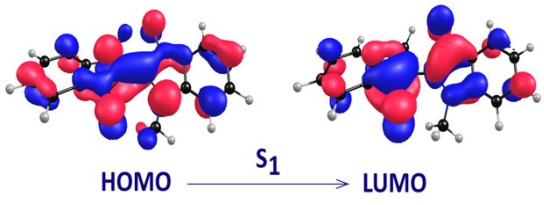


Fig. SI3 (**A**) Simulated spectra from TDDFT for NC_1Ind in MCH, THF and DMSO, (**B**) Excitation and emission values in eV, (**C**) Simulated spectra from TDDFT for N,NC_1Ind in THF and (D) π π* main contribution to S_1

Table SI2 - Spectroscopic properties, including wavelength maxima for absorption (λ_{Abs}) and fluorescence (λ_{Fluo}) and Stoke shift (Δ_{SS}) for the *N*-alkyl indigo derivatives in *n*-dodecane, MCH, 2MeTHF, EtOH, MeOH, DMF and DMSO solutions at T = 293 K. For indigo the same parameters are also presented in 2MeTHF, DMF and DMSO for comparison. The solvent properties (viscosity η in cP and dielectric constant ε) are also given.

Compound	Solvent	η (cP)	ε'	λ_{Abs} (nm)	λ_{Fluo} (nm)	Δ_{SS}[a] (cm^{-1})
Ind	**2MeTHF**	0.575	7.58	602	631	763
	DMF	0.924	36.71	610	653	1080
	DMSO	1.991	46.45	619	665	1117
NC_1Ind	***n*-dodecane**	1.508	2.015	619	653	841
	MCH	0.975	2.023	617	653	894
	2MeTHF	0.575	7.58	622	670	1152
	EtOH	1.200	24.55	627	699	1643
	MeOH	0.593	32.66	628	699	1617
	DMF	0.924	36.71	630	690	1380
	DMSO	1.991	46.45	635	700	1462
NC_2Ind	***n*-dodecane**	1.508	2.015	625	654	709
	MCH	0.975	2.023	624	656	782
	2MeTHF	0.575	7.58	629	671	995
	EtOH	1.200	24.55	632	700	1537
	MeOH	0.593	32.66	632	700	1537
	DMF	0.924	36.71	637	690	1206
	DMSO	1.991	46.45	641	700	1315
NC_3Ind	***n*-dodecane**	1.508	2.015	629	659	724
	MCH	0.975	2.023	627	658	751
	2MeTHF	0.575	7.58	631	671	945
	EtOH	1.200	24.55	636	699	1417
	MeOH	0.593	32.66	636	699	1442
	DMF	0.924	36.71	639	691	1178
	DMSO	1.991	46.45	644	700	1242
NC_6Ind	***n*-dodecane**	1.508	2.015	629	660	747
	MCH	0.975	2.023	628	658	726
	2MeTHF	0.575	7.58	632	672	942
	EtOH	1.200	24.55	636	699	1417
	MeOH	0.593	32.66	636	699	1458
	DMF	0.924	36.71	639	691	1178
	DMSO	1.991	46.45	644	702	1283

Table SI2 (continued)

Compound	Solvent	η (cP)	ε'	λ_{Abs} (nm)	λ_{Fluo} (nm)	Δ_{SS}[a] (cm^{-1})
NC_8Ind	***n*-dodecane**	1.508	2.015	629	658	701
	MCH	0.975	2.023	628	658	726
	2MeTHF	0.575	7.58	632	673	964
	EtOH	1.200	24.55	636	699	1417
	MeOH	0.593	32.66	636	701	1458
	DMF	0.924	36.71	639	692	1199
	DMSO	1.991	46.45	644	702	1283
$NC_{12}Ind$	***n*-dodecane**	1.508	2.015	630	659	699
	MCH	0.975	2.023	628	658	726
	2MeTHF	0.575	7.58	632	673	964
	EtOH	1.200	24.55	636	696	1355
	MeOH	0.593	32.66	637	697	1351
	DMF	0.924	36.71	639	691	1178
	DMSO	1.991	46.45	644	703	1303
$NC_{18}Ind$	***n*-dodecane**	1.508	2.015	630	659	699
	MCH	0.975	2.023	628	658	726
	2MeTHF	0.575	7.58	632	673	964
	EtOH	1.200	24.55	636	698	1397
	MeOH	0.593	32.66	636	700	1438
	DMF	0.924	36.71	640	692	1174
	DMSO	1.991	46.45	644	704	1323

[a]Δ_{SS} = Stokes' shift.

Table SI3 - Spectroscopic properties including wavelength maxima for absorption (λ_{Abs}) and fluorescence (λ_{Fluo}) and Stoke shift (Δ_{SS}) for the *N,N'*-dialkyl indigo derivatives in *n*-dodecane, MCH, 2MeTHF, DMF and DMSO solutions at T = 293 K. The solvent properties (viscosity η in cP and dielectric constant **ε**) are also given.

Compound	Solvent	η (cP)	ε'	λ_{Abs} (nm)	λ_{Fluo} (nm)	Δ_{SS}[a] (cm^{-1})
	***n*-dodecane**	1.508	2.015	629	664	838
	MCH	0.975	2.023	628	664	863
N,N'C_1Ind	**2MeTHF**	0.575	7.58	637	683	1057
	DMF	0.924	36.71	648	712	1387
	DMSO	1.991	46.45	655	726	1493
	***n*-dodecane**	1.508	2.015	639	683	1008
	MCH	0.975	2.023	639	685	1051
N,N'C_2Ind	**2MeTHF**	0.575	7.58	649	708	1284
	DMF	0.924	36.71	660	739	1620
	DMSO	1.991	46.45	667	750	1650
	***n*-dodecane**	1.508	2.015	642	691	1105
	MCH	0.975	2.023	642	691	1105
N,N'C_3Ind	**2MeTHF**	0.575	7.58	653	707	1170
	DMF	0.924	36.71	665	740	1524
	DMSO	1.991	46.45	672	752	1583
	***n*-dodecane**	1.508	2.015	642	693	1146
	MCH	0.975	2.023	643	693	1122
N,N'C_6Ind	**2MeTHF**	0.575	7.58	654	707	1146
	DMF	0.924	36.71	664	739	1528
	DMSO	1.991	46.45	672	751	1565
	***n*-dodecane**	1.508	2.015	642	692	1125
	MCH	0.975	2.023	645	694	1095
N,N'C_8Ind	**2MeTHF**	0.575	7.58	653	708	1190
	DMF	0.924	36.71	664	740	1547
	DMSO	1.991	46.45	672	751	1565
	***n*-dodecane**	1.508	2.015	645	692	1053
	MCH	0.975	2.023	645	693	1074
N,N'C_{12}Ind	**2MeTHF**	0.575	7.58	652	708	1233
	DMF	0.924	36.71	665	739	1506
	DMSO	1.991	46.45	672	751	1565
	***n*-dodecane**	1.508	2.015	644	692	1077
	MCH	0.975	2.023	646	693	1050
N,N'C_{18}Ind	**2MeTHF**	0.575	7.58	654	712	1246
	DMF	0.924	36.71	666	739	1483
	DMSO	1.991	46.45	673	751	1543

[a]Δ_{SS} = Stokes' shift.

Table SI4 - Photophysical properties including fluorescence quantum yields (ϕ_F), lifetimes (τ_F) and rate constants (k_F, k_{NR}) for the *N*-alkyl indigo derivatives and indigo itself in different organic solvents at T = 293 K.

Compound	Solvent	ϕ_F	τ_F (ns^{-1})[b]	k_F (ns^{-1})[c]	k_{NR} (ns^{-1})[c]
Ind[a]	**2MeTHF**	0.0019	0.128	0.0148	7.79
	DMF	0.0023	0.135	0.0170	7.39
	DMSO	0.0019	0.117	0.0162	8.53
NC_1Ind	***n*-dodecane**	0.0006	0.032	0.0203	31.61
	MCH	0.0006	0.032	0.0179	30.94
	2MeTHF	0.0010	0.066	0.0152	15.09
	EtOH	0.0003	N.D.	N.D.	N.D.
	MetOH	0.0003	N.D.	N.D.	N.D.
	DMF	0.0009	N.D.	N.D.	N.D.
	DMSO	0.0008	N.D.	N.D.	N.D.
NC_2Ind	***n*-dodecane**	0.0007	0.042	0.0171	23.76
	MCH	0.0006	0.034	0.0189	29.74
	2MeTHF	0.0010	0.067	0.0144	15.02
	EtOH	0.0003	N.D.	N.D.	N.D.
	MetOH	0.0003	N.D.	N.D.	N.D.
	DMF	0.0009	N.D.	N.D.	N.D.
	DMSO	0.0008	N.D.	N.D.	N.D.
NC_3Ind	***n*-dodecane**	0.0007	0.039	0.0186	25.56
	MCH	0.0006	0.036	0.0177	27.84
	2MeTHF	0.0010	0.067	0.0143	14.96
	EtOH	0.0003	N.D.	N.D.	N.D.
	MetOH	0.0003	N.D.	N.D.	N.D.
	DMF	0.0009	N.D.	N.D.	N.D.
	DMSO	0.0008	N.D.	N.D.	N.D.
NC_6Ind	***n*-dodecane**	0.0007	0.038	0.0191	26.44
	MCH	0.0007	0.037	0.0203	27.38
	2MeTHF	0.0010	0.069	0.0144	14.52
	EtOH	0.0003	N.D.	N.D.	N.D.
	MetOH	0.0003	N.D.	N.D.	N.D.
	DMF	0.0010	N.D.	N.D.	N.D.
	DMSO	0.0008	N.D.	N.D.	N.D.

Table SI4 (continued)

Compound	Solvent	ϕ_F	τ_F (ns^{-1})[b]	k_F (ns^{-1})[c]	k_{NR} (ns^{-1})[c]
	***n*-dodecane**	0.0008	0.039	0.0199	25.95
	MCH	0.0007	0.040	0.0178	24.73
	2MeTHF	0.0010	0.074	0.0138	13.45
NC_8Ind	**EtOH**	0.0003	N.D.	N.D.	N.D.
	MetOH	0.0003	N.D.	N.D.	N.D.
	DMF	0.0010	N.D.	N.D.	N.D.
	DMSO	0.0009	N.D.	N.D.	N.D.
	***n*-dodecane**	0.0008	0.039	0.0208	25.55
	MCH	0.0007	0.039	0.0182	25.36
	2MeTHF	0.0010	0.076	0.0128	13.09
NC_{12}Ind	**EtOH**	0.0003	N.D.	N.D.	N.D.
	MetOH	0.0003	N.D.	N.D.	N.D.
	DMF	0.0010	N.D.	N.D.	N.D.
	DMSO	0.0009	N.D.	N.D.	N.D.
	***n*-dodecane**	0.0008	0.039	0.0203	25.56
	MCH	0.0008	0.039	0.0198	25.56
	2MeTHF	0.0010	0.072	0.0145	13.80
NC_{18}Ind	**EtOH**	0.0003	N.D.	N.D.	N.D.
	MetOH	0.0003	N.D.	N.D.	N.D.
	DMF	0.0011	N.D.	N.D.	N.D.
	DMSO	0.0009	N.D.	N.D.	N.D.

[a] For Indigo, the values were taken from ref.[1]. [b] $\tau_{F\,=}\,\tau_2$ (Table SI6). [c] N.D.= Not determined. [d] $k_F = \frac{\phi_F}{\tau_F}$; $k_{NR} = \frac{1-\phi_F}{\tau_F}$.

Table SI5 - Photophysical properties including fluorescence quantum yields (ϕ_F), lifetimes (τ_F) and rate constants (k_F, k_{NR}) for the *N,N'*-dialkyl indigo derivatives and indigo itself in different organic solvents at T = 293 K.

Compound	Solvent	ϕ_F	τ_F (ns^{-1})[a]	k_F (ns^{-1})[b]	k_{NR} (ns^{-1})[b]
	***n*-dodecane**	0.0389	2690	0.0145	0.36
	MCH	0.0286	2044	0.014	0.48
N,N'C_1Ind	**2MeTHF**	0.0014	76.6	0.0183	13.04
	DMF	0.0003	N.D.	N.D.	N.D.
	DMSO	0.0002	N.D.	N.D.	N.D.

Table SI5 (continued)

Compound	Solvent	ϕ_F	τ_F (ns^{-1})[a]	k_F (ns^{-1})[b]	k_{NR} (ns^{-1})[b]
N,N'C_2Ind	***n*-dodecane**	0.0137	1064	0.0129	0.93
	MCH	0.0094	957	0.0098	1.04
	2MeTHF	0.0007	62.2	0.0112	16.00
	DMF	0.0005	N.D.	N.D.	N.D.
	DMSO	0.0002	N.D.	N.D.	N.D.
N,N'C_3Ind	***n*-dodecane**	0.014	1522	0.0092	0.65
	MCH	0.0089	1341	0.0066	0.74
	2MeTHF	0.0009	73.8	0.0122	13.53
	DMF	0.0004	N.D.	N.D.	N.D.
	DMSO	0.0002	N.D.	N.D.	N.D.
N,N'C_6Ind	***n*-dodecane**	0.0107	1692	0.0063	0.58
	MCH	0.0068	1325	0.0051	0.75
	2MeTHF	0.001	101.5	0.0094	9.84
	DMF	0.0004	N.D.	N.D.	N.D.
	DMSO	0.0003	N.D.	N.D.	N.D.
N,N'C_8Ind	***n*-dodecane**	0.0102	1540	0.0066	0.64
	MCH	0.0079	1286	0.0061	0.77
	2MeTHF	0.0012	98.8	0.0121	10.11
	DMF	0.0005	N.D.	N.D.	N.D.
	DMSO	0.0003	N.D.	N.D.	N.D.
N,N'C_{12}Ind	***n*-dodecane**	0.0135	1651	0.0082	0.6
	MCH	0.0135	1374	0.0098	0.72
	2MeTHF	0.0088	115.7	0.0761	8.57
	DMF	0.0005	N.D.	N.D.	N.D.
	DMSO	0.0003	N.D.	N.D.	N.D.
N,N'C_{18}Ind	***n*-dodecane**	0.0141	1761	0.008	0.56
	MCH	0.0073	1425	0.0051	0.7
	2MeTHF	0.001	123.3	0.0081	8.1
	DMF	0.0004	N.D.	N.D.	N.D.
	DMSO	0.0003	N.D.	N.D.	N.D.

[a] $\tau_{F} = \tau_2$ (Table SI7). [b] $k_F = \frac{\phi_F}{\tau_F}$; $k_{NR} = \frac{1-\phi_F}{\tau_F}$.

Table SI6 - Time resolved fluorescence data for *N*-alkyl indigo derivatives (λ_{exc} = 433 nm) in *n*-dodecane, MCH and 2MeTHF at T = 293 K. For indigo the same parameters are also presented in DMF for comparison.

Coumpond	λ_{exc} (nm)	Solvent	λ_{em} (nm)	τ_1 (ps)	τ_2 (ps)	a_1	a_2	χ^2
Ind[a]	378	**DMF**	630	10.4	135.5	0.61	0.39	1.1
			660			-0.51	1.00	1.03
NC_1Ind	433	***n*-dodecane**	650		31.6		1.00	1.15
		MCH	650		32.3		1.00	1.03
		2MeTHF	670	10.8	66.2	-0.70	1.00	1.17
NC_2Ind		**n-dodecane**	655		42.1		1.00	1.02
		MCH	655		33.6		1.00	1.04
		2MeTHF	670	10.4	66.5	-0.93	1.00	1.11
NC_3Ind		***n*-dodecane**	660	7.2	39.1	-0.77	1.00	1.20
			710			-0.79	1.00	1.25
		MCH	660	9.5	35.9	-0.78	1.00	1.03
			710			-0.94	1.00	1.31
		2MeTHF	670	10.8	66.8	-0.88	1.00	1.00
			710			-0.93	1.00	1.15
NC_6Ind		***n*-dodecane**	660	8.5	37.8	-0.98	1.00	1.01
		MCH	660	7.8	36.5	-0.95	1.00	1.03
		2MeTHF	670	9.1	68.8	-0.59	1.00	1.44
NC_8Ind		***n*-dodecane**	660	9.8	38.5	-0.84	1.00	1.04
			710			-0.89	1.00	1.17
		MCH	670	7.2	40.4	-0.72	1.00	1.20
			720			-0.76	1.00	1.57
		2MeTHF	660	12.7	74.3	-0.94	1.00	1.18
			710			-1.07	1.00	1.34
NC_{12}Ind		***n*-dodecane**	670	9.8	39.1	-0.75	1.00	1.00
			700			-0.94	1.00	1.07
		MCH	670	10.1	39.4	-0.57	1.00	1.31
			720			-0.86	1.00	1.25
		2MeTHF	670	10.1	76.3	-0.78	1.00	1.62
			710			-0.77	1.00	1.32
NC_{18}Ind		***n*-dodecane**	670	10.4	39.1	-0.78	1.00	1.08
			700			-1.08	1.00	1.19
		MCH	660	9.8	39.1	-0.75	1.00	1.00
			710			-0.94	1.00	1.07
		2MeTHF	670	12.7	72.4	-0.29	1.00	1.02
			710			-1.06	1.00	1.09

[a]For indigo data from ref.[1]

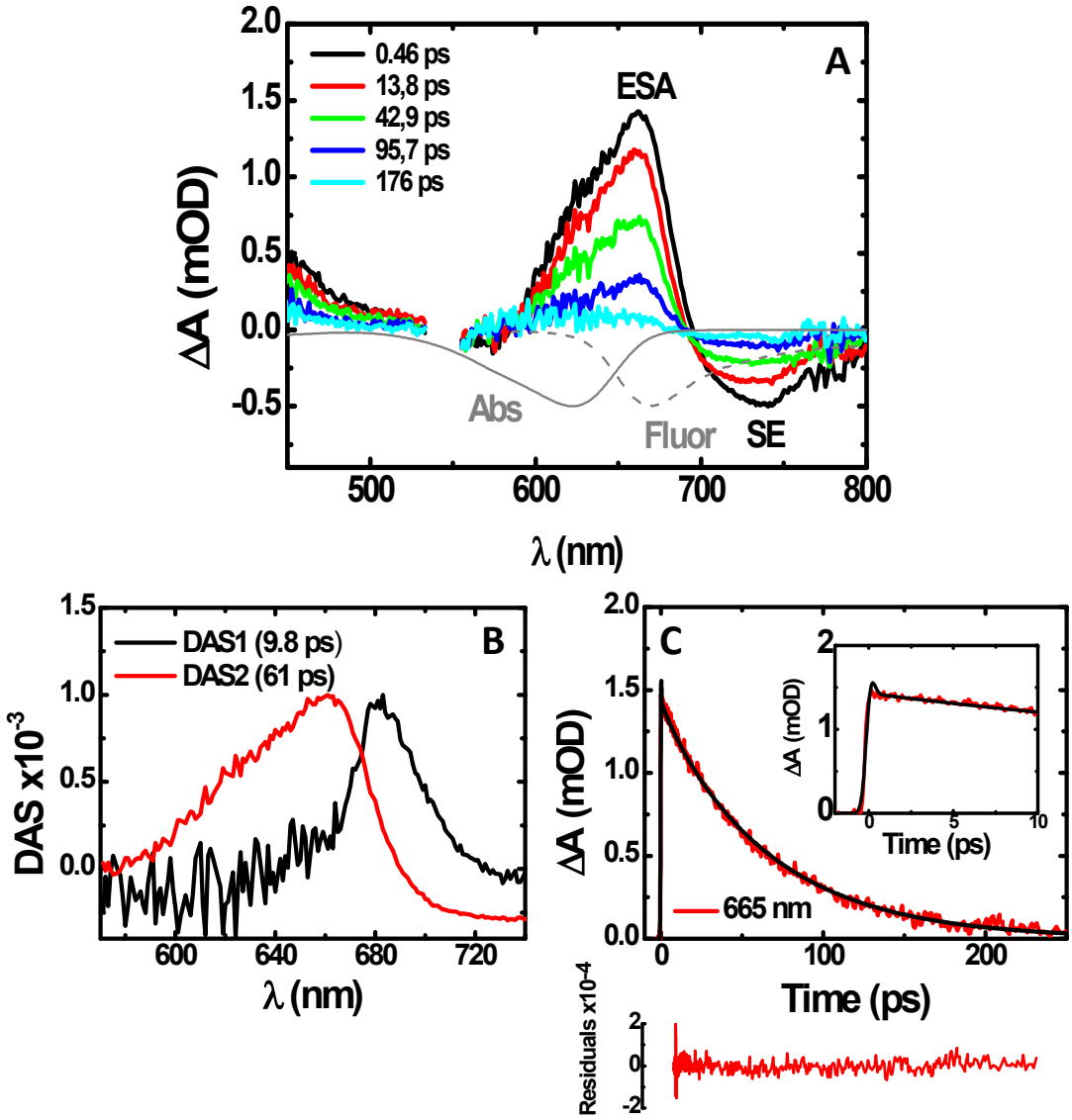


Fig. SI4 Room temperature femtosecond time-resolved transient absorption data for NC_1Ind in 2MeTHF solution obtained with λ_{exc} = 550 nm (**A**), decay associated species (**B**) and kinetic traces with fits from the global analysis of the TA data (**C**). Also shown are the weighted residuals values for a better judgment of the quality of the fits. The inverted ground-state absorption and fluorescence emission spectra are also presented for comparison purposes. The 530-570 nm spectral range is not presented because it is dominated by the scattered pump beam (550 nm).

Table SI7 - Time resolved fluorescence data for *N,N'*-dialkyl indigo derivatives (λ_{exc} = 433 nm or λ_{exc} = 451 nm) in *n*-dodecane, MCH and 2MeTHF at T = 293 K.

Coumpond	λ_{exc} (nm)	Solvent	λ_{em} (nm)	τ_1 (ps)	τ_2 (ps)	a_1	a_2	χ^2
N,N'C_1Ind	451	***n*-dodecane**	660		2689.5		1.00	1.21
		MCH	660		2044.0		1.00	1.14
		2MeTHF	690		76.6		1.00	1.32
N,N'C_2Ind	433	***n*-dodecane**	690	308.7	1064.0	0.29	0.71	1.11
			790			0.33	0.67	1.60
	451	**MCH**	690	269	956.8	0.40	0.60	1.24
		2MeTHF	710		62.4		1.00	1.06
N,N'C_3Ind	433	***n*-dodecane**	690	430.9	1522.2	0.26	0.74	1.18
			790			0.31	0.69	1.62
		MCH	690	363	1341.0	0.31	0.69	1.36
			790			0.37	0.63	1.80
	451	**2MeTHF**	710		73.8		1.00	1.23
N,N'C_6Ind	433	***n*-dodecane**	690	540.3	1692.2	0.32	0.68	1.23
			790			0.35	0.65	1.76
	451	**MCH**	690	278.7	1325.2	0.27	0.73	1.11
		2MeTHF	710		101.5		1.00	1.10
N,N'C_8Ind	451	***n*-dodecane**	690	344	1540	0.26	0.74	1.00
		MCH	690	189	1286	0.27	0.73	1.60
		2MeTHF	710		98.8		1.00	1.01
N,N'C_{12}Ind	433	***n*-dodecane**	690	405.5	1651.1	0.23	0.77	1.11
			790			0.28	0.72	1.74
	451	**MCH**	694	270.6	1374.1	0.26	0.74	1.20
		2MeTHF	710		115.7		1.00	1.50
N,N'C_{18}Ind	433	***n*-dodecane**	690	474.8	1760.6	0.28	0.72	1.18
			790			0.32	0.68	1.13
	451	**MCH**	694	257.5	1424.6	0.27	0.73	1.18
		2MeTHF	710		123.3		1.00	1.00

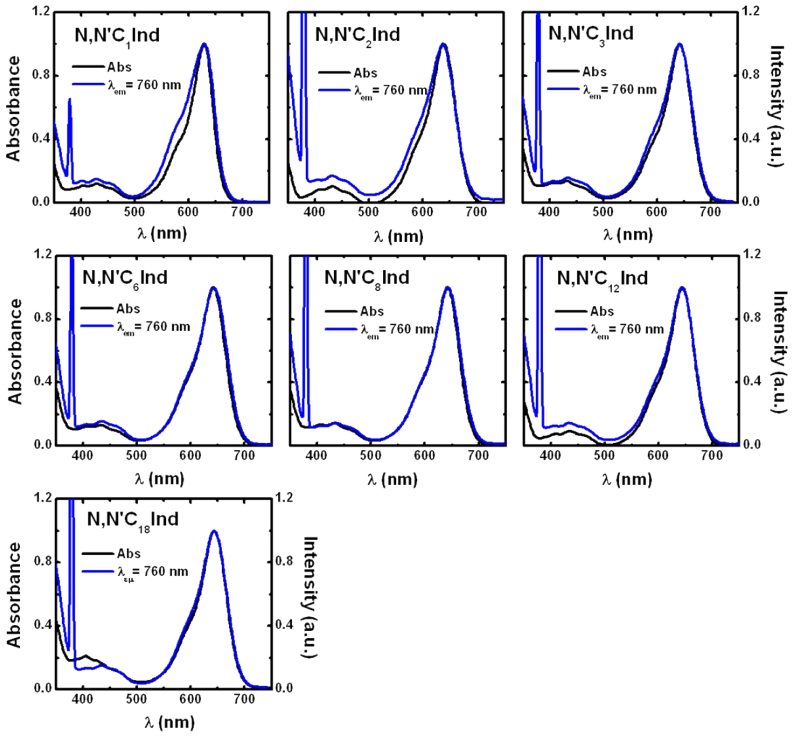


Fig. SI5 Normalized absorption and excitation spectra of *N,N'*-dialkyl indigo derivatives in *n*-dodecane solutions at T = 293 K.

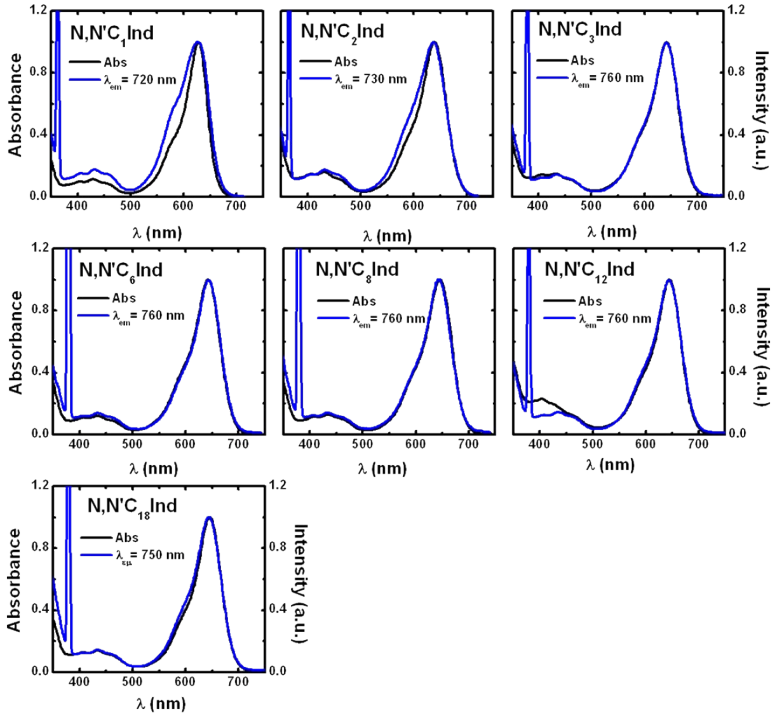


Fig. SI6 Normalized absorption and excitation spectra of *N,N'*-dialkyl indigo derivatives in MCH solutions at T = 293 K.

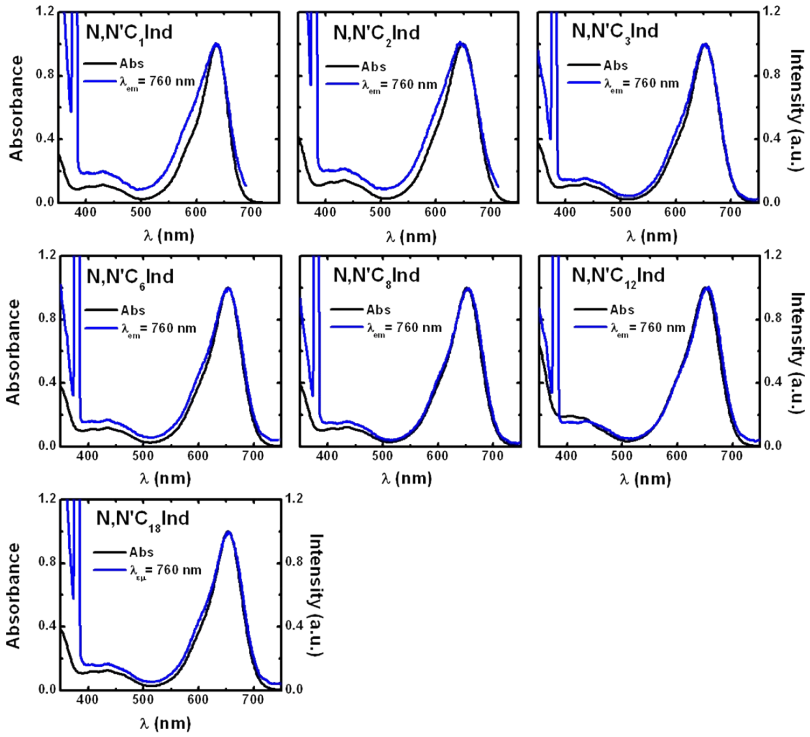


Fig. SI7 Normalized absorption and excitation spectra of *N,N'*-dialkyl indigo derivatives in 2MeTHF solutions at T = 293 K.

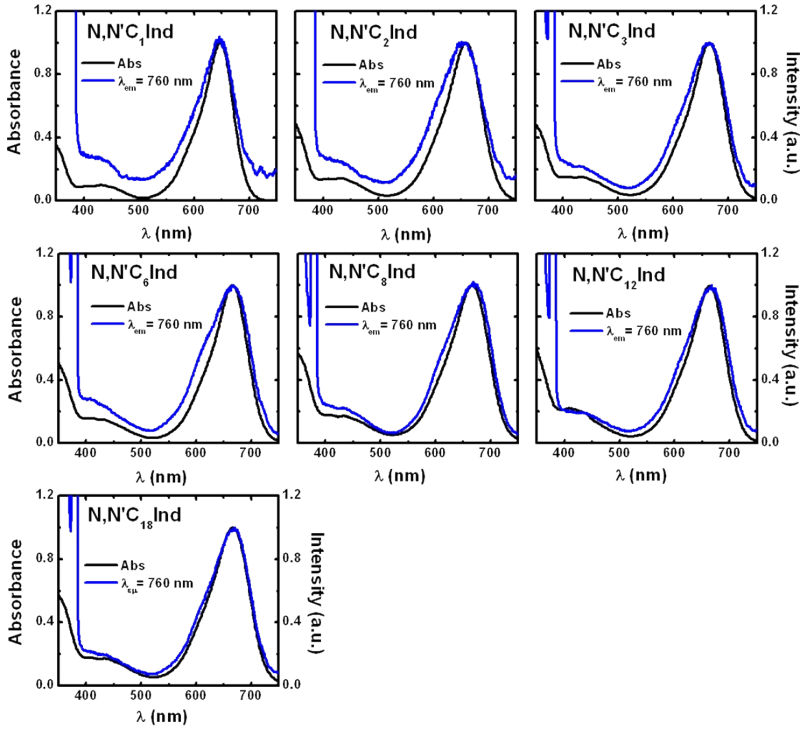


Fig. SI8 Normalized absorption and excitation spectra of *N,N'*-dialkyl indigo derivatives in DMF solutions at T = 293 K.

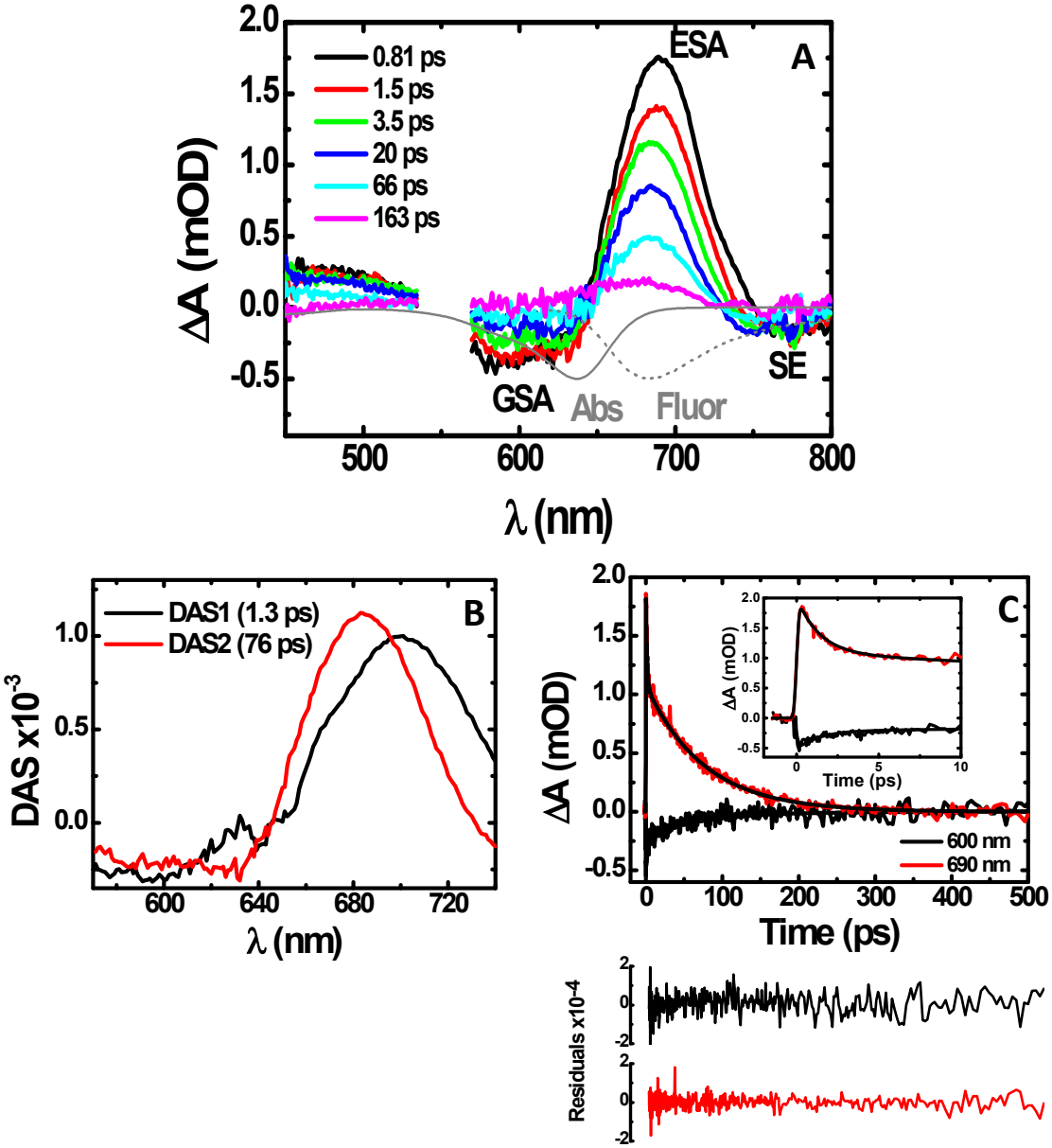


Fig. SI9 Room temperature femtosecond time-resolved transient absorption data for N,N'C_1Ind in 2MeTHF solution obtained with λ_{exc}= 550 nm (**A**), decay associated species (**B**) and kinetic traces with fits from the global analysis of the TA data (**C**). Also shown are the weighted residuals values for a better judgment of the quality of the fits. The inverted ground-state absorption and fluorescence emission spectra are also presented for comparison purposes. The 530-570 nm spectral range is not presented because it is dominated by the scattered pump beam (550 nm).

References

1. J. Pina, D. Sarmento, M. Accoto, P. L. Gentili, L. Vaccaro, A. Galvão and J. S. Seixas de Melo, *J. Phys. Chem. B*, 2017, **121**, 2308-2318.