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Amide-Based Molecular Knots as Platforms for Fluorescent Switches

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Abstract: A series of amide-based molecular knots equipped selectively with fluorescent dansyl and/or pyrenesulfonyl moieties were synthesized from the readily available tris(allyloxy)knotane. UV/Vis absorption spectra, emission spectra, and the emission lifetimes of the fluorescent knotanes were investigated in chloroform at 298 K. The absorption spectra of the knotanes correspond to those of mixtures of their UV-active constituents. The fluorescence quantum yields and lifetimes of the dansyl and pyrenesulfonyl moieties are partly quenched by the knotane platform. In the **KN**(**Da**)$_2$(**Py**) species, the fluorescent excited state of the dansyl units ($\lambda_{max}=510$ nm) lies at lower energy than the fluorescent excited state of the pyrenesulfonyl unit ($\lambda_{max}=385$ nm), the emission of which is accordingly quenched with sensitization of the dansyl fluorescence. In the **KN**(**Ao**)$_2$(**Da**), **KN**(**Ao**)(**Da**)$_2$, and **KN**(**Da**)$_3$ species, the addition of acids causes the protonation of their dansyl units with a consequent decrease in the intensity of the dansyl band at 510 nm and appearance of the emission band of the protonated dansyl unit ($\lambda_{max}=340$ nm). Each dansyl unit of **KN**(**Ao**)(**Da**)$_2$ and **KN**(**Da**)$_3$ undergoes the independent protonation. In these incompletely protonated knotanes the fluorescence of the protonated dansyl units is partly quenched by nonprotonated ones. These processes can be quantitatively reversed upon addition of a base. In **KN**(**Da**)$_2$(**Py**), an increase of the fluorescence of its pyrenesulfonyl group is observed when the dansyl groups are protonated. The results obtained show that the readily available and easily functionalizable amide-knotanes can be used as an interesting scaffold to obtain fluorescent switches.

Keywords: energy transfer · fluorescence · molecular knots · protonation · supramolecular chemistry

Introduction

Molecular knots[1] (*knotanes*) are unique representatives of intertwined molecules. Their synthesis had been a challenging task until recent templation methods led to noticeable advances enabling, for example, the preparation of the amide-knotane **KN** on multigram scale.[2,3]

Knotane **KN** is a three-nanometer scaffold with restricted conformational flexibility.[1e,2d] The knotane can be selectively functionalized with different groups at three predetermined sites of the molecule periphery.[2] Thus, a selectively functionalized *covalent* knotane is formally comparable with a metal ion capable of *coordinating* three ligands resulting in homo- or heteroleptic metal complexes. Inspired by this constitutional analogy, we have prepared homo- and heteroleptic knotanes and we have investigated the ground and excited state electronic interaction among the various components.

Starting from **KN**(**Ao**)$_3$, a variety of substituents can be appended to the **KN** scaffold. We have investigated the fluorescent properties of the **KN**(**Ao**)$_2$(**Da**), **KN**(**Ao**)(**Da**)$_2$, **KN**(**Da**)$_3$, **KN**(**Ao**)$_2$(**Py**), and **KN**(**Da**)$_2$(**Py**) knots, that carry dansyl and/or pyrenesulfonyl fluorescent units. For the sake of comparison, the fluorescence properties of reference compounds for the dansyl and pyrenesulfonyl moieties, **Da** and **Py**, have also been examined.

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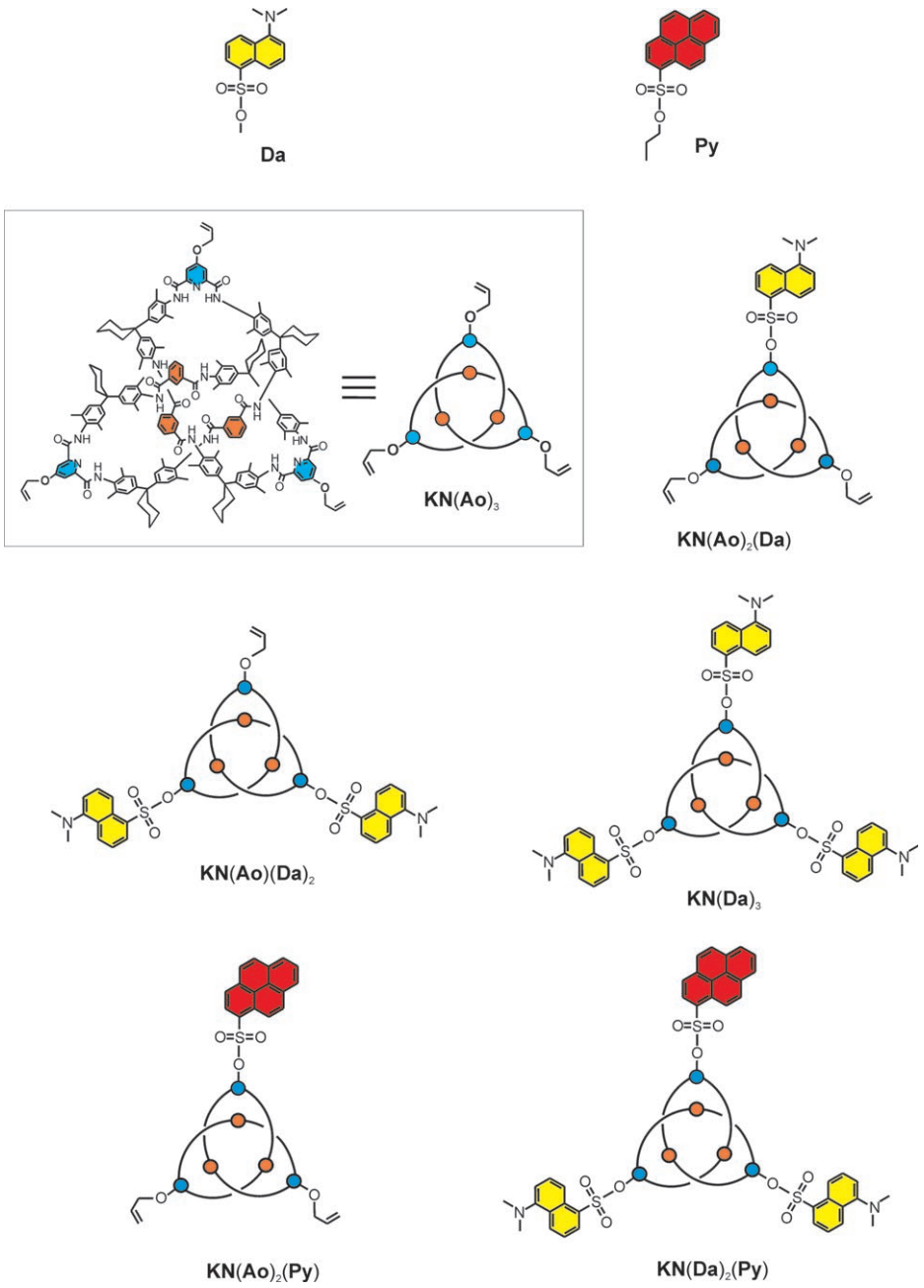

Results and Discussion

Absorption and emission spectra: Tris(allyloxy)knotane **KN(Ao)$_3$** does not exhibit any significant absorption above 350 nm and shows no emission. Figure 1 shows the absorption spectra of **KN(Ao)$_2$(Da)**, **KN(Ao)$_2$(Py)** and the reference dansyl (**Da**) and pyrensulfonyl (**Py**) compounds. As seen, in both cases the absorption spectra of the knotanes are slightly red-shifted relative to those of the reference compounds. Their fluorescence spectra (Figure 2) are also slightly red-shifted and partly quenched. Notably, the emission spectrum of **KN(Ao)$_2$(Py)** is considerably less structured and more intense above 425 nm than that of the reference compound **Py**, with a weak and broad band in the 400–500 nm region that overlaps the structured emission of the **Py** moiety (Figure 2).

In the case of **KN(Ao)$_2$(Da)**, the emission quantum yield decreases from 0.40 for the **Da** reference compound to 0.005, and the lifetime drops from 15.3 ns to less than 1 ns (Table 1). Since the knotane does not show any energy level lower than the fluorescent excited state of dansyl, the most likely quenching mechanism appears to be electron transfer from pyridine to the dansyl excited state. The excitation spectrum (emission at 500 nm) showed that the light absorbed by the intense band of the knotane below 350 nm does not contribute to the fluorescence intensity of the **Da** moiety.

In line with our expectations, the absorption spectra of **KN(Ao)(Da)$_2$** and **KN(Da)$_3$** contain proportionally increasing intensity of the dansyl band relative to **KN(Ao)$_2$(Da)**. The fluorescence spectra and the emission quantum yields of the bis- and trisdansyloxy knotanes are the same as those of the monodansylated derivative **KN(Ao)$_2$(Da)** (Table 1).

In the case of **KN(Ao)$_2$(Py)**, the emission quantum yield decreases from 0.30 for the **Py** reference compound to 0.20; the light absorbed by the knotane scaffold (excitation <350 nm) does not contribute to the fluorescence band of the knot. The pyrenesulfonyl reference compound **Py** exhibits a single exponential decay (7.2 ns), whereas **KN(Ao)$_2$(Py)** shows a double exponential decay (4.3 and 1.4 ns). This result, together with the shape of the band (Figure 2), indicates that emission of **KN(Ao)$_2$(Py)** originates from two distinct excited states, namely the fluorescent excited state of the pyrensulfonyl moiety and a lower-energy excited state that can be assigned to an exciplex formed by interaction of the pyrenesulfonyl excited state with a pyridine unit of the knotane. The longer lifetime has to be related to the exciplex emission, since its contribution increases on moving towards the tail of the emission band.

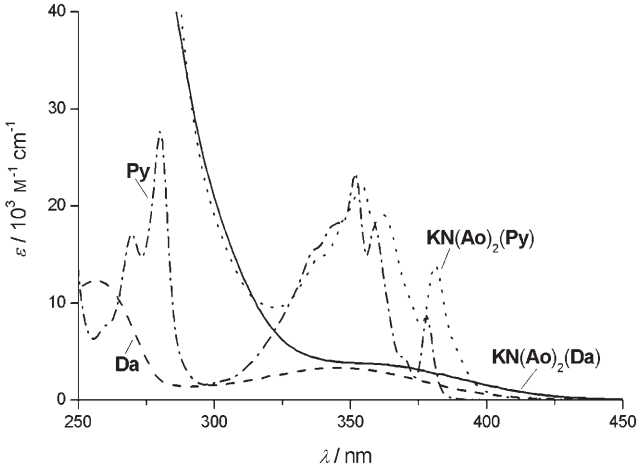

Figure 1. Absorption spectra of **KN(Ao)$_2$(Da)** (solid line), **KN(Ao)$_2$(Py)** (dotted line) and the reference dansyl (**Da**, dashed line) and pyrenesulfonyl (**Py**, dashed dotted line) compounds in chloroform at 298 K.

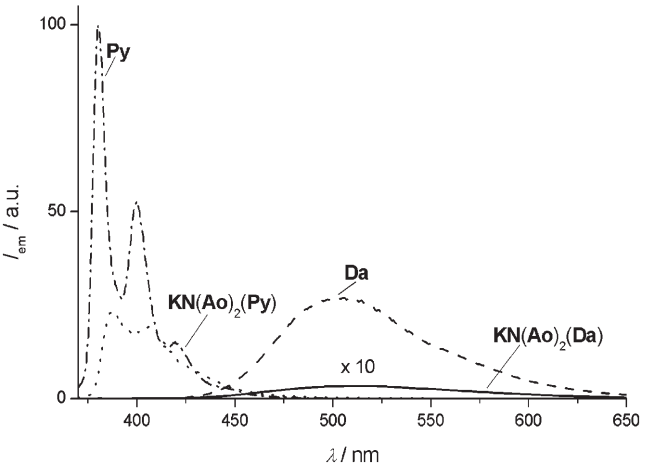

Figure 2. Emission spectra of **KN(Ao)$_2$(Da)** (solid line), **KN(Ao)$_2$(Py)** (dotted line) and the reference dansyl (**Da**, dashed line) and pyrenesulfonyl (**Py**, dashed dotted line) compounds in chloroform at 298 K. Excitation at 350 nm of isoabsorbing solutions.

Table 1. Luminescence quantum yields and lifetimes in chloroform solution at 298 K.

	Φ_{em}	τ [ns]		Φ_{em}	τ [ns]
Da	0.40	15.3	**Py**	0.30	7.2
KN(Ao)$_2$(Da)	0.005	<0.5	**KN(Ao)$_2$(Py)**	0.20	1.4, 4.3[a]
KN(Ao)(Da)$_2$	0.005	<0.5	**KN(Da)$_2$(Py)**	0.10	0.9[b]
KN (Da)$_3$	0.005	<0.5			

[a] Above 500 nm. [b] Predominant component at 420 nm of a multiexponential decay.

Figure 3 shows the absorption and emission spectra of the compound that contains two dansyl and one pyrenesulfonyl substituents, **KN(Da)$_2$(Py)**, and, for comparison purposes, those of **KN(Ao)$_2$(Py)**. The absorption spectrum of **KN(Da)$_2$(Py)** in the 320–450 nm region is dominated by the intense bands of the pyrenesulfonyl unit, but there is also a clear contribution around 350 nm by the two dansyl units.

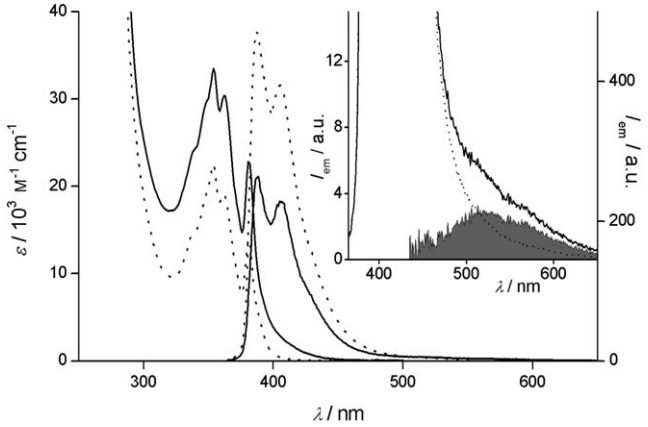

Figure 3. Absorption and emission spectra of **KN(Da)$_2$(Py)** (solid line) and **KN(Ao)$_2$(Py)** (dotted line) in chloroform at 298 K. Excitation wavelength: 354 nm. Inset shows the dansyl emission band, obtained by subtraction of normalized emission spectra of **KN(Da)$_2$(Py)** and **KN(Ao)$_2$(Py)**.

As far as the emission spectrum is concerned (excitation at 354 nm), the pyrene band is clearly present and in its tail a weak dansyl band can also be detected (Figure 3, inset). Quantitative comparison, after correction for the fraction of absorbed light by the various moieties, shows that the emission intensities of the pyrenesulfonyl unit decreases from 0.20 to 0.10 in going from **KN(Ao)$_2$(Py)** to **KN(Da)$_2$(Py)**, and that the intensity of the dansyl band in **KN(Da)$_2$(Py)** is at least 1.5 times more intense than that observed for **KN(Ao)$_2$(Da)**. This result indicates that a relatively efficient (ca. 50 %) energy transfer from the excited pyrenesulfonyl moiety to the dansyl units takes place. For **KN(Da)$_2$(Py)**, the fluorescence intensity shows a multiexponential decay, with a predominant contribution of a 0.9 ns component at 420 nm.

Protonation of the dansyl moieties: It is known[4] that the amino group of the dansyl chromophoric unit can be quantitatively protonated by trifluoromethylsulfonic (triflic) acid in organic solvents, with strong changes in the absorption and emission spectra. We have found that both reference compound **Da** and the dansyl moieties of **KN(Ao)$_2$(Da)**, **KN(Ao)(Da)$_2$**, and **KN(Da)$_3$** exhibit such spectral changes.[5] Upon protonation, the characteristic absorption band of the dansyl chromophoric group at 350 nm disappears and a shoulder arises around 295 nm; at the same time, the dansyl emission band at 500 nm progressively disappears, being replaced by the naphthalene-like emission of the **DaH$^+$** moiety with maximum at about 340 nm (see, e.g., Figure 4).[6] The process is quantitatively reversed upon addition of a base. Since the normalized ([H$^+$] per dansyl unit) changes in the absorption intensities of the titration plots practically coincide with those observed for the reference compound **Da**, each dansyl unit of **KN(Ao)(Da)$_2$** and **KN(Da)$_3$** undergoes independent protonation. It should also be noted that the titration plots obtained from the decrease in the absorption and emission bands of the **Da** moiety coin-

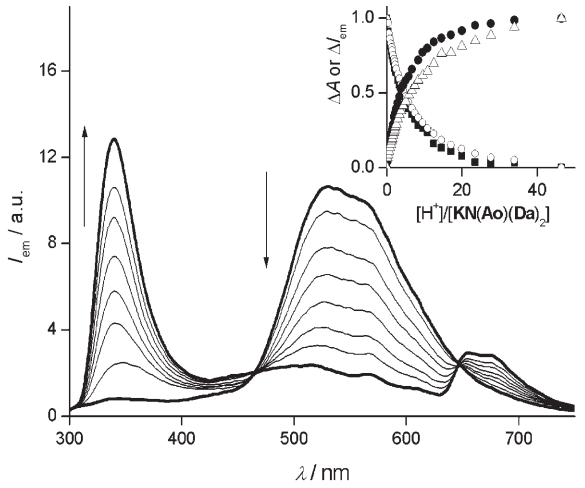

Figure 4. Changes in the emission spectrum of **KN**(**Ao**)(**Da**)$_2$ in chloroform upon addition of triflic acid. Excitation at 278 nm (isosbestic point). The band at 680 nm is an artifact, due to the second harmonic of the band at 340 nm. Inset shows the normalized absorption (294 nm ● and 360 nm ■) and emission (340 nm △ and 530 nm ○) titration profile.

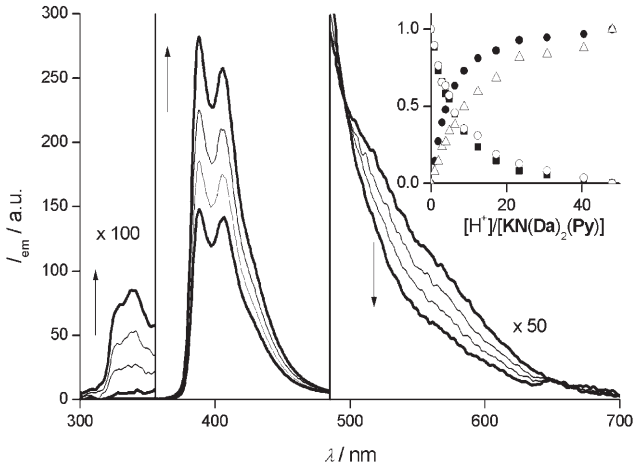

Figure 5. Changes in the emission spectrum of **KN**(**Da**)$_2$(**Py**) in chloroform upon addition of triflic acid. Excitation at 278 nm (isosbestic point). Inset shows the normalized absorption (294 nm ● and 360 nm ■) and emission (340 nm △ and 530 nm ○) titration profile.

cide, while those obtained from the increase in the **Da**H$^+$ emission band is less steep than the corresponding increase in the **Da**H$^+$ absorption band (see, e.g., Figure 4 inset). This result shows that, when both **Da** and **Da**H$^+$ are present in the same knot, the fluorescence of **Da**H$^+$ is partly quenched, whereas that of the **Da** moiety is unaffected. By contrast, mutual quenching of the two types of excited moieties had been previously observed in the acid titration of polydansyl dendrimers in which the two chromophoric groups are much closer.

We have also verified that the absorption and fluorescence spectra of the pyrenesulfonyl derivative **KN**(**Ao**)$_2$(**Py**) are not affected by addition of acid.

In the case of **KN**(**Da**)$_2$(**Py**), the addition of triflic acid causes changes in the absorption spectrum consistent with protonation of the dansyl moieties. The changes in the emission spectrum (Figure 5) indicate that, as expected, the band of the dansyl unit around 500 nm disappears and the band of the protonated dansyl at 340 nm arises; these changes are accompanied by a noticeable increase in intensity of the pyrene band at around 400 nm. It should be noted that, while the decrease of dansyl fluorescence intensity is accompanied by a parallel decrease of the dansyl absorption band, the increase in intensity of the protonated dansyl emission at 340 nm is less steep than expected from the fraction of protonated dansyl units, as estimated from the increase of the **Da**H$^+$ absorption at 294 nm (Figure 5, inset). The increase of the protonated dansyl emission is accompanied by an increase of pyrene fluorescence intensity: this result is not only to the disappearance of the **Da** moieties that quench the excited **Py** unit (vide supra), but also to sensitization of the pyrene emission by the excited **Da**H$^+$ moieties. Indeed, protonation causes a switching in the energy level of the dansyl unit, as schematically shown by the energy level diagram of Figure 6. The overlap of the absorption

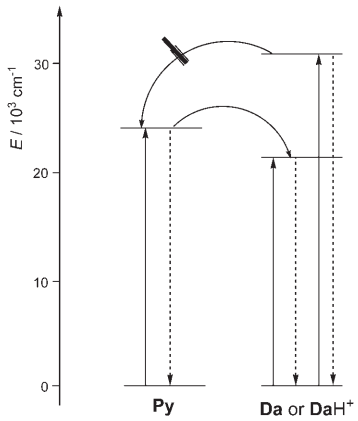

Figure 6. Schematic diagram of the relevant energy levels involved in the described absorption and emission bands of **KN**(**Da**)$_2$(**Py**) and **KN**(**Da**H$^+$)$_2$(**Py**). For the sake of clarity, radiationless decay has been omitted.

bands of the three chromophoric groups does not allow us to draw quantitative conclusions, although the apparent lack of quenching of the weak **Da**H$^+$ emission (Figure 5) suggests that energy transfer from the excited **Da**H$^+$ moieties to the **Py** unit does not occur, perhaps because of the very short lifetime of the donor.

Conclusion

We have investigated the photophysical properties of the **KN**(**Ao**)$_2$(**Da**), **KN**(**Ao**)(**Da**)$_2$, **KN**(**Da**)$_3$, **KN**(**Ao**)$_2$(**Py**), and **KN**(**Da**)$_2$(**Py**) compounds obtained by selective peripheral functionalization of amide-knotane (**KN**) with dansyl (**Da**), and pyrenesulfonyl (**Py**) units. In a formal way, the selectively functionalized nanometric knotane platform can be compared with a metal ion capable of coordinating three ligands. Indeed, it is possible to prepare homo- and heteroleptic

knotane derivatives in a similar way as homo- and heteroleptic metal complexes.[7] The analogy can be further pursued: 1) there is an interaction between the appended chromophoric groups and the knotane platform, as in the case of ligands with metal;[8] 2) in heteroleptic knotane derivatives there can be electronic interaction between two different chromophoric units, as may happen between two different ligands in heteroleptic metal complexes.[9]

The **KN(Ao)$_2$(Da)**, **KN(Ao)(Da)$_2$**, **KN(Da)$_3$**, **KN(Ao)$_2$(Py)**, and **KN(Da)$_2$(Py)** knotanes show interesting fluorescent properties. Knotanes **KN(Ao)$_2$(Da)**, **KN(Ao)(Da)$_2$**, **KN(Da)$_3$** exhibit the characteristic dansyl fluorescence, strongly quenched by the scaffold. Upon addition of acid, the dansyl moieties undergo protonation with replacement of the **Da** fluorescence ($\lambda_{max}=510$ nm) with the higher energy **DaH$^+$** emission ($\lambda_{max}=340$ nm). In **KN(Ao)$_2$(Py)**, the fluorescent band of the pyrenesulfonyl unit is unaffected by acid addition, but partly quenched because of exciplex formation. In the case of **KN(Da)$_2$(Py)**, an energy-transfer process from the pyrenesulfonyl to the dansyl units occurs, but, upon protonation of the dansyl moieties, switching of the energy levels takes place (the energy of the pyrenesulfonyl excited state lies above that of dansyl and below that of protonated dansyl, Figure 6). As a consequence, the intensity of the pyrene band increases.

When the energy of the fluorescent level of a unit can be displaced by an external input, switching in the direction of energy transfer processes can be obtained.[10] Even more interesting, of course, would be fully heteroleptic nano-sized species made of three, suitably designed appended units.

Experimental Section

Synthesis: Tris(allyloxy)knotane **KN(Ao)$_3$** was synthesized by our previously reported procedure.[2a] The preparation of the new fluorescent knotanes **KN(Ao)$_2$(Da)**, **KN(Ao)(Da)$_2$**, **KN(Da)$_3$**, **KN(Ao)$_2$(Py)**, and **KN(Da)$_2$(Py)**, in turn, follows the selective deprotection–sulfonylation strategy.[2c]

The methods for preparation of tris(allyloxy)knotane (**KN(Ao)$_3$**) and bis(dansyloxy)allyloxyknotane (**KN(Ao)(Da)$_2$**) were previously reported by us.[2a,b] Model compound, 5-(dimethylamino)-1-naphthalenesulfonic acid methyl ester (**Da**) was synthesized according to the literature procedure.[11]

Dansyloxybis(allyloxy)knotane (KN(Ao)$_2$(Da)): Dansyl chloride (14 mg, 0.051 mmol) dissolved in dry dichloromethane (2 mL) was added to a stirred suspension containing bis(allyloxy)monohydroxyknotane[2a] (60 mg, 0.021 mmol) and triethylamine (0.1 mL, 0.7 mmol) in dry dichloromethane (10 mL). The reaction mixture was stirred at reflux for two hours and the solvent was then removed under reduced pressure. The crude product was purified by a column chromatography on silica gel with CH_2Cl_2/ethylacetate (10:1) eluent. Yield: 60 mg (93%); m.p. 266°C; ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=0.05$ (s, 3H; CH_3), 0.85 (s, 3H; CH_3), 0.96 (s, 6H; CH_3), {1.24, 1.36, 1.47, 1.48, 1.57, 1.60, 1.82 (br), 1.99, 2.18, 2.25 2.26, 2.28, 2.32} (144H; CH_2, CH_3), 2.86 (s, 6H; NCH_3), 4.88 (m, 4H; OCH_2), 4.99 (t, $J=7$ Hz, 1H; ArH), 5.32–5.48 (m, 4H; CH_2=CH), 5.84 (d, $J=7$ Hz, 1H; ArH), 6.07 (m, 2H; CH=CH_2), {6.41, 6.44, 6.51, 6.64, 6.80, 6.89, 6.96, 7.16, 7.20, 7.33, 7.36, 7.38, 7.44, 7.51, 7.55, 7.57, 7.68, 7.76, 7.77, 7.79, 7.80, 7.81, 7.82, 7.86, 7.87, 7.88, 7.90, 7.92, 8.28, 8.29, 8.30, 8.67 (d, J(H,H)=8 Hz, 1H)} (ArH), {8.27, 8.58, 9.05, 9.13, 9.32, 9.36, 9.41, 9.56, 9.77, 10.19, 10.21, 10.48, 10.51, 10.99, 11.00, 11.03, 11.06 ppm} (NH); FAB MS: m/z: 3079.40 [M+H]$^+$; calcd monoisotopic peak ($^{12}C_{195}{}^1H_{209}{}^{14}N_{16}{}^{16}O_{17}{}^{32}S$): 3078.56.

Tris(dansyloxy)knotane KN(Da)$_3$: Dansyl chloride (40 mg, 0.15 mmol) dissolved in dry acetonitrile (5 mL) was added to a stirred solution of trihydroxy-knotane **7** (40 mg, 0.015 mmol) and triethylamine (0.2 g, 2 mmol) in dry acetonitrile (10 mL). The reaction mixture was stirred at room temperature for two hours and the solvent was then evaporated under reduced pressure. The crude product was purified by a column chromatography on silica gel with CH_2Cl_2/ethylacetate (20:3). Yield: 44 mg (72%); m.p. 232°C; ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=0.02$ (s, 3H; CH_3), 0.83 (s, 3H; CH_3), 0.89 (s, 3H; CH_3), 0.92 (s, 3H; CH_3), {1.24, 1.31, 1.33, 1.44, 1.52, 1.59 (br), 1.79 (br), 1.93, 2.13, 2.16, 2.21, 2.26, 2,29} (144H; CH_2, CH_3), 2.86 (s, 18H; NCH_3), 4.94 (t, $J=7$ Hz, 1H; ArH), 5.27 (s, 1H; ArH), 5.79 (d, $J=7$ Hz, 1H; ArH), {6.41, 6.42, 6.48, 6.60, 6.62, 6.79 (br), 6.88, 6.94, 6.96, 7.15, 7.32, 7.36, 7.38, 7.42, 7.49, 7.51, 7.52, 7.56, 7.64–7.69, 7.75–7.89, 8.26, 8.27, 8.28, 8.30, 8.67 (d, J(H,H)=8 Hz, 3H)} (ArH), {8.24, 8.56, 9.05, 9.12, 9.33, 9.39, 9.77, 10.12, 10.49, 10.53, 10.97, 11.00 ppm} (12H; NH); FAB MS: m/z: 3466.70 [M+H]$^+$; calcd monoisotopic peak ($^{12}C_{213}{}^1H_{223}{}^{14}N_{18}{}^{16}O_{21}{}^{32}S_3$): 3464.60.

Pyrenesulfonyloxybis(allyloxy)knotane KN(Ao)$_2$(Py): Pyrenesulfonyl chloride (22 mg, 0.073 mmol) dissolved in dry dichloromethane (2 mL) was added to a stirred solution of bis(allyloxy)monohydroxyknotane[2a] (60 mg, 0.021 mmol) and triethylamine (0.1 mL, 0.7 mmol) in dry acetonitrile (10 mL). The reaction mixture was stirred at room temperature for two hours and the solvent was then removed under reduced pressure. The crude product was purified by a column chromatography on silica gel with CH_2Cl_2/ethylacetate (10:1) eluent. Yield: 63 mg (89%); m.p. 279°C; ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=0.05$ (s, 3H; CH_3), 0.85 (s, 3H; CH_3), 0.95 (s, 6H; CH_3), {1.24, 1.35, 1.44, 1.56, 1.82 (br), 1.88, 1.99, 2.08, 2.18, 2.25 2.26, 2.28, 2.31} (144H; CH_2 and CH_3), 4.87 (m, 4H; OCH_2), 4.98 (t, ^3J(H,H)=7 Hz, 1H; ArH), 5.31–5.47 (m, 4H; CH_2=H), 5.81 (d, ^3J(H,H)=7 Hz, 1H; ArH), 6.08 (m, 2H; CH=H_2), {6.41, 6.44, 6.51, 6.64, 6.80, 6.89, 6.96, 7.16, 7.20, 7.33, 7.36, 7.38, 7.44, 7.51, 7.55, 7.57, 7.68, 7.76, 7.77, 7.79, 7.80, 7.81, 7.82, 7.86, 7.87, 7.88, 7.90, 7.92, 8.28–8.67, 8.70 (d, ^3J(H,H)=8 Hz, 1H; ArH), 8.96 (d, ^3J(H,H)=9.2 Hz, 1H; ArH)} (ArH), {8.26, 8.57, 9.05, 9.12, 9.31, 9.35, 9.41, 9.56, 9.78, 10.20, 10.42, 10.48, 10.52, 10.92, 10.96, 10.99, 11.00 ppm} (NH); FAB MS: m/z: 3109.50 [M+H]$^+$; calcd monoisotopic peak ($^{12}C_{199}{}^1H_{206}{}^{14}N_{15}{}^{16}O_{17}{}^{32}S$): 3109.56.

Pyrenesulfonyloxybis(dansyloxy)knotane KN(Da)$_2$(Py): Pyrenesulfonyl chloride (11 mg, 0.036 mmol) dissolved in dry acetonitrile (5 mL) was added to a stirred solution of hydroxylbis(dansyloxy)knotane[2a] (40 mg, 0.012 mmol) and triethylamine (0.2 g, 2 mmol) in dry acetonitrile (10 mL). The reaction mixture was stirred at room temperature for two hours and the solvent was then evaporated under reduced pressure. The crude product was purified by a column chromatography on silica gel with CH_2Cl_2/ethylacetate (20:3). Yield: 34 mg (82%); m.p. 190°C; ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=0.05$ (s, 3H; CH_3), 0.85 (s, 3H; CH_3), 0.96 (s, 6H; CH_3), {1.24, 1.36, 1.47, 1.48, 1.57, 1.60, 1.82 (br), 1.99, 2.18, 2.25 2.26, 2.28, 2.32} (144H; CH_2 and CH_3), 2.86 (s, 12H; NCH_3), {4.98 (t, $J=7$ Hz, 1H), 5.25 (s, 1H) 5.78 (d, $J=7$ Hz, 1H), 6.41, 6.44, 6.51, 6.64, 6.80, 6.89, 6.96, 7.16, 7.20, 7.33, 7.36, 7.38, 7.44, 7.51, 7.55, 7.57, 7.68, 7.76, 7.77, 7.79, 7.80, 7.81, 7.82, 7.86, 7.87, 7.88, 7.90, 7.92, 8.28, 8.29, 8.30, 8.67 (d, J(H,H)=8 Hz, 1H), 8.70 (d, ^3J(H,H)=8 Hz, 1H; ArH), 8.96 (d, ^3J(H,H)=9.2 Hz, 1H; ArH)} (ArH), {8.23, 8.57, 9.03, 9.11, 9.29, 9.36, 9.39, 9.74, 10.08, 10.11, 10.41, 10.45, 10.49, 10.91, 10.94, 10.96, 11.00 ppm} (NH); MALDI-TOF MS: m/z: 3495.88 [M+H]$^+$; calcd monoisotopic peak ($^{12}C_{217}{}^1H_{220}{}^{14}N_{17}{}^{16}O_{21}{}^{32}S_3$): 3495.58.

Pyrenesulfonic acid *n*-propyl ester (Py): Pyrenesulfonyl chloride (50 mg, 0.17 mmol) dissolved in dry *n*-propanol (3 mL) was injected into a stirred 10% solution of sodium propanolate in *n*-propanol (30 mL). (The solution of sodium propanolate was freshly prepared by dissolving sodium in dry *n*-propanol.) The reaction mixture was then heated at 50°C for 3 h. The mixture was reduced in volume to 10 mL, poured into water (100 mL) and extracted with dichloromethane (2×70 mL). The solvent was dried over Mg_2SO_4 and evaporated in vacuum. The crude product was purified on silica gel with dichloromethane/ethylacetate (20:1) eluant resulting in a colorless solid. Yield: 51 mg (79%); m.p. 149°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.82$ (t, ^3J(H,H)=7.4 Hz, 3H; CH_3), 1.62 (m, 2H;

CH_2), 4.00 (t, ^3J(H,H) = 6.6 Hz, 3H; CH_3), 8.12–8.16 (m, 2H; ArH), 8.24 (d, ^3J(H,H) = 8.2 Hz, 1H; ArH), 8.26 (d, ^3J(H,H) = 8.2 Hz, 1H; ArH), 8.33–8.37 (m, 3H; ArH), 8.70 (d, ^3J(H,H) = 8 Hz, 1H; ArH), 8.94 ppm (d, ^3J(H,H) = 9.2 Hz, 1H; ArH); ^{1}H NMR (125 MHz, $CDCl_3$): δ = 10.01, 22.32, 72.53, 123.65, 123.75, 123.88, 125.17, 127.01, 127.02, 127.20, 127.21, 127.69, 127.77, 128.86, 130.27, 130.39, 130.74, 130.94, 135.52 ppm; elemental analysis calcd (%) for $C_{19}H_{16}O_3S$ (324.39): C 70.35, H 4.97, S 9.88; found: C 70.32, H 4.70, S 9.95.

Photophysical experiments: All the experiments were carried out in chloroform at room temperature (298 K). Equipment used for recording absorption, emission, and excitation spectra and for measuring emission lifetime have been previously described.[12] Fluorescence quantum yields were measured following the methods of Demas and Crosby[13] (standard used: anthracene in ethanol, $\Phi = 0.27$[14]). When necessary, correction for the fraction of absorbed light was performed.

Acid titrations were monitored by changes in absorption and emission spectra. In the latter case, excitation was performed in an isosbestic point of the **Da** and **Da**H^+ units (278 nm).

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[1] a) G. Schill, *Catenanes, Rotaxanes and Knots*, Academic Press, New York, **1971**; b) J.-P. Sauvage, C. Dietrich-Buchecker, *Molecular Catenanes, Rotaxanes and Knots, A Journey Through the World of Molecular Topology*, Wiley-VCH, Weinheim, **1999**; c) C. Dietrich-Buchecker, B. X. Colasson, J. P. Sauvage, *Top. Curr. Chem.* **2005**, *249*, 261; d) S. J. Cantrill, K. S. Chichack, A. J. Peters, J. F. Stoddart, *Acc. Chem. Res.* **2005**, *38*, 1; e) O. Lukin, F. Vögtle, *Angew. Chem.* **2005**, *117*, 1480; *Angew. Chem. Int. Ed.* **2005**, *44*, 1456.

[2] a) O. Lukin, J. Recker, A. Böhmer, W. M. Müller, T. Kubota, Y. Okamoto, M. Nieger, R. Fröhlich, F. Vögtle, *Angew. Chem.* **2003**, *115*, 458; *Angew. Chem. Int. Ed.* **2003**, *42*, 442; b) O. Lukin, T. Kubota, Y. Okamoto, F. Schelhase, A. Yoneva, W. M. Müller, U. Müller, F. Vögtle, *Angew. Chem.* **2003**, *115*, 4681; *Angew. Chem. Int. Ed.* **2003**, *42*, 4542; c) O. Lukin, W. M. Müller, U. Müller, A. Kaufmann, C. Schmidt, J. Leszczynski, F. Vögtle, *Chem. Eur. J.* **2003**, *9*, 3507; d) C. A. Schalley, W. Reckien, S. Peyerimhoff, B. Baytekin, F. Vögtle, *Chem. Eur. J.* **2004**, *10*, 4777.

[3] a) O. Safarowsky, M. Nieger, R. Fröhlich, F. Vögtle, *Angew. Chem.* **2000**, *112*, 1699; *Angew. Chem. Int. Ed.* **2000**, *39*, 1616; b) F. Vögtle, A Hünten, E. Vogel, S. Buschbeck, O. Safarowsky, J. Recker, A. Parham, N. Knott, W. M. Müller, U. Müller, Y. Okamoto, T. Kubota, W. Lindner, E. Francotte, S. Grimme, *Angew. Chem.* **2001**, *113*, 2534; *Angew. Chem. Int. Ed.* **2001**, *40*, 2468.

[4] H. F. M. Nelissen, F. Venema, R. M. Uittenbogaard, M. C. Feiters, R. J. M. Nolte, *J. Chem. Soc. Perkin Trans. 2* **1997**, 2045.

[5] In principle, pyridine could also undergo protonation, but in this compound the nitrogen atom is expected to be engaged in hydrogen bonds with the amidic hydrogen atoms. Indeed, we did not find any evidence of pyridine protonation.

[6] F. Vögtle, S. Gestermann, C. Kauffmann, P. Ceroni, V. Vicinelli, L. De Cola, V. Balzani, *J. Am. Chem. Soc.* **1999**, *121*, 12161.

[7] A. Juris, S. Campagna, V. Balzani, G. Gremaud, and A. von Zelewsky, *Inorg. Chem.* **1988**, *27*, 3652.

[8] V. Balzani in *Handbook of Photochemistry*, 3rd ed. (Eds.: M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi), Taylor & Francis, CRC, New York, **2006**, Chapter 2.

[9] A. Vogler, H. Kunkely, *Top. Curr. Chem.* **2001**, *213*, 143.

[10] S. A. de Silva, K. C. Loo, B. Amorelli, S. L. Pathirana, M. Nyakirang'ani, M. Dharmasena, S. Demarais, B. Dorcley, P. Pullay, Y. A. Salih, *J. Mater. Chem.* **2005**, *15*, 2791.

[11] H. J. Kallmayer, P. Schwarz, *Pharmazie* **1989**, *44*, 119.

[12] G. Bergamini, P. Ceroni, V. Balzani, F. Vögtle, S.-K. Lee, *ChemPhysChem* **2004**, *5*, 315.

[13] J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991.

[14] *Handbook of Photochemistry*, 3rd ed. (Eds.: M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi), Taylor & Francis, CRC, New York **2006**, Chapter 10.

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