ELECTRONIC SUPPLEMENTARY INFORMATION

Remarkable Influence of '*Phane Effect*' on the Excited-State Properties of Cofacially-Oriented Coumarins

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parameters	Cou-Nap	Cou-Dur
Empirical formula	C ₃₀ H ₂₀ O ₄	$C_{20} H_{20} O_2$
Formula weight	444.46	292.36
Temperature (K)	293(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Solvent of crystallization	CHCl ₃ /hexane	CHCl ₃ /hexane
Crystal habit	Block	Block
Crystal color	Colorless	Colorless
Crystal system	Orthorhombic	Triclinic
Space group	P 2 ₁ 2 ₁ 2 ₁	P-1
a (Å)	9.008(5)	11.798(5)
b (Å)	15.383(5)	12.109(5)
c (Å)	15.627(5)	12.211(5)
α (deg)	90.000(5)	95.007(5)
β (deg)	90.000(5)	102.009(5)
γ (deg)	90.000(5)	110.256(5)
Volume (Å ³)	2165.4(16)	1576.5(11)
Z	4	4
Calculated density (mg/m ³)	1.363	1.232
Absorption coefficient (mm ⁻¹)	0.090	0.078
F(000)	928	624
θ range for data collection (°)	2.61 to 28.30	2.08 to 28.43
Index ranges	$-12 \le h \le 12$	$-15 \le h \le 15$
	$-20 \le k \le 20$	-16 ≤ k ≤ 16
	$-20 \le l \le 20$	$-16 \le l \le 16$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.015	0.975
Final R indices [I>2sigma(I)]	$R_1 = 0.0580,$	$R_1 = 0.0834,$
	$wR_2 = 0.0947$	$wR_2 = 0.2180$
R indices (all data)	$R_1 = 0.1288,$	$R_1 = 0.1462,$
	$wR_2 = 0.1123$	$wR_2 = 0.2558$
CCDC deposition number	1509578	1509579

 Table S1. Crystal data of Cou-Nap and Cou-Dur.



Figure S1. Thermal ellipsoid plot of **Cou-Nap** (contour probability = 50%).



Figure S2. Thermal ellipsoid plot of **Cou-Dur** (contour probability = 50%).

Determination of Onsager Cavity Radius for Cou-Nap

The van der Waals volume (V_{vdW}) of **Cou-Nap** was estimated theoretically by using the atomic and bond contributions of van der Waals volume (VABC). According to Abraham and coworkers,¹ the van der Waals volume (Å³/molecule) can be calculated from the following formula:

$$V_{vdw} = \sum (\text{all atom contributions}) - 5.92N_{\text{B}} - 14.7R_{\text{A}} - 3.8R_{\text{NA}}$$

where, $N_{\rm B}$ is the number of bonds, $R_{\rm A}$ is the number of aromatic rings, and $R_{\rm NA}$ is the number of non-aromatic rings.

If the total number of atoms in the molecule is N, then the number of bonds present (N_B) can be calculated using the relation:

$$N_{\rm B} = N - 1 + R_{\rm A} + R_{\rm NA}$$

The van der Waals volumes (V_{vdW}) for carbon, hydrogen and oxygen are considered to be as 20.58, 7.24 and 14.71 Å³, respectively.¹ For **Cou-Nap**, the molecular formula is C₃₀H₂₀O₄. Thus, the sum of all atom contribution for this molecule turns out to be:

 $\Sigma(\text{all atom contributions}) = (30 \times 20.58) + (20 \times 7.24) + (4 \times 14.71)$ = 617.4 + 144.8 + 58.84= 821.04

The number of bonds present in the molecule is given by:

$$N_{\rm B} = N - 1 + R_{\rm A} + R_{\rm NA}$$

= (30 + 20 + 4) - 1 + 6 + 0
= 59

Thus, the calculated van der Waals volume (V_{vdW} in Å³) for **Cou-Nap** should be given by:

$$V_{vdw} = \sum (\text{all atom contributions}) - 5.92N_{\text{B}} - 14.7 R_{\text{A}} - 3.8 R_{\text{NA}}$$

= 821.04 - (5.92 × 59) - (14.7 × 6) - (3.8 × 0)
= 821.04 - 349.28 - 88.2
= 383.56

Now, if we consider the Onsager radius to be 'a' (in Å) assuming a spherical model, then the van der Waals volume (V_{vdW} in Å³) can be regarded as,

$$V_{\nu dW} = \frac{4}{3}\pi a^3$$

Thus, for Cou-Nap, the relation turns out to be,

$$\frac{4}{3}\pi a^3 = 383.56$$

i.e., $a^3 = 383.56 \times \frac{3}{4\pi} = 91.57$
Thus, $a = 4.51$ Å

Table S2. Calculated van der Waals Volume and Onsager Cavity Radius for Cou-Nap.

Parameters	Cou-Nap
molecular formula	$C_{30}H_{20}O_4$
\sum (all atom contributions)	821.04
N _B	59
van der Waals volume: $V_{\rm vdW}$ (Å ³)	383.56
Onsager cavity radius: a (Å)	4.51

Determination of Ground and Excited-State Dipole Moments of Cou-Nap

The ratio of excited state (μ_e) and ground state (μ_g) dipole moments can be determined by applying the Bakshiev formulation (Eq. 1) and Chamma and Viallet equations (Eq. 2).^{2,3} The assumptions with these formulations are the following: (i) μ_e and μ_g are almost collinear, (ii) the solute molecule is modeled as a spherical cavity with a rigid dipole at the centre, (iii) the cavity radius remains the same in both ground and excited states and (iv) the molecular aspects of solvation are ignored.³

In accordance with the Bakshiev formulation,

$$\bar{v}_a - \bar{v}_f = \frac{2(\mu_e - \mu_g)^2}{a^3 h c} f_1(D, n) + constant$$
$$= S_1 f_1(D, n) + constant \qquad \dots \dots Eq. 1$$

where, the slope of the linear fit of $(\bar{v}_a - \bar{v}_f)$ versus $f_1(D, n)$ is expressed as:

$$S_1 = \frac{2(\mu_e - \mu_g)^2}{a^3 hc}$$

Further, in accordance with the Chamma and Viallet equations,

$$\frac{\left(\bar{v}_{a}+\bar{v}_{f}\right)}{2} = -\frac{2\left(\mu_{e}^{2}-\mu_{g}^{2}\right)}{a^{3}hc}f_{2}(D,n) + constant$$
$$= S_{2}f_{2}(D,n) + constant \qquad \dots \dots Eq.2$$

where, the slope of the linear fit of $\frac{(\bar{v}_a + \bar{v}_f)}{2}$ versus $f_2(D, n)$ is expressed as:

$$S_2 = -\frac{2(\mu_e^2 - \mu_g^2)}{a^3 hc}$$

Here, \bar{v}_a and \bar{v}_f are, respectively, the absorption and fluorescence maxima and *n*, *D*, *a*, *B*, *c* and *h* stands for refractive indices, dielectric constants of the solvents, Onsager cavity radius, properties of betaine dye, velocity of light and Planck's constant, respectively.

The polarity functions f_1 and f_2 can be expressed as:

$$f_1(D,n) = \left[\frac{D-1}{D+2} - \frac{n^2 - 1}{n^2 + 2}\right] \left(\frac{2n^2 + 1}{n^2 + 2}\right) \dots \dots Eq.3$$
$$f_2(D,n) = \frac{1}{2} f_1(D,n) + \frac{3}{2} \frac{(n^4 - 1)}{(n^2 + 2)^2} \dots \dots Eq.4$$

In Table S3 are shown the numerical values of the functions f_1 and f_2 for different solvents.

solvent	D ^a	n ^a	$f_1(D,n)^b$	$f_2(D,n)^c$	$E_{\mathrm{T}}^{\mathrm{N}d}$
cyclohexane	2.01	1.424	0.036	0.290	0.006
benzene	2.28	1.498	0.005	0.340	0.111
1,4-dioxane	2.21	1.420	0.05	0.311	0.164
ethyl acetate	6.02	1.370	0.489	0.498	0.228
dimethylformamide	36.7	1.427	0.834	0.709	0.386
acetonitrile	37.5	1.342	0.865	0.666	0.460
ethanol	24.5	1.359	0.813	0.652	0.654
methanol	32.6	1.326	0.855	0.650	0.762

Table S3. Properties and Polarity Functions of Different Solvents.

^{*a*} Values taken from ref. 4. ^{*b*} Calculated from Eq. 3. ^{*c*} Calculated from Eq. 4. ^{*d*} Values taken from ref. 5.

From the linear regressions of the solvatochromic shifts with f_1 and f_2 , one can find the slopes to be: $S_1 = 2227.15$ and $S_2 = -3191.06$. Thus, the ratio of the dipole moment in the excited and ground state $\left(\frac{\mu_e}{\mu_g}\right)$ turns out to be 5.61 using Eq. 5.

$$\frac{\mu_e}{\mu_g} = \frac{|S_1 - S_2|}{|S_1 + S_2|} \quad \dots \dots Eq.5$$

Further, the solvatochromic Stokes shifts of **Cou-Nap** can be fitted linearly (slope = m) with the Reichardt's solvent polarity parameter $(E_T^N)^5$ using the empirical correlation developed by Radhakrishan and co-workers (Eq. 6).⁶

$$\bar{v}_a - \bar{v}_f = 11307.6 \left[\left(\frac{\Delta \mu_c}{\Delta \mu_B} \right)^2 \left(\frac{a_B}{a_C} \right)^3 \right] E_T^N + constant$$
$$= m E_T^N + constant \qquad \dots \dots Eq.6$$

The slope (i.e., m) of the linear fit of $(\bar{v}_a - \bar{v}_f)$ versus E_T^N is expressed as:

$$m = 11307.6 \left[\left(\frac{\Delta \mu_C}{\Delta \mu_B} \right)^2 \left(\frac{a_B}{a_C} \right)^3 \right]$$

Here, $\Delta \mu_{\rm B}$ (= 9 D) and $a_{\rm B}$ (= 6.2 Å) designate the dipole moment change on excitation and Onsager radius, respectively, for betaine dye as the probe.³ Similarly, the terms $\Delta \mu_{\rm C}$ and $a_{\rm C}$ are the corresponding values for **Cou-Nap**. As mentioned earlier, the Onsager radius of the latter, i.e., $a_{\rm C}$, was estimated to be ca. 4.51 Å based on calculation of Van der Waals volume (383.56 Å³) using the method developed by Abraham and co-workers. Thus, by plugging in the value of the slope, m = 4005.80, one can readily calculate the difference of the excited and ground state dipole moments ($\Delta \mu_{\rm C}$) to be 3.32 D.

Thus, given the ratio of 5.61 and the difference of 3.32 D, the experimental value of the ground and excited state dipole moments of **Cou-Nap**, thus, turn out to be ca. 0.72 D and 4.04 D, respectively.



Figure S3. Temperature effect on the fluorescence spectra (left) and quantum yields (right) of **Cou-Nap** in acetonitrile and methanol. Notice that there is hardly in any change in the fluorescence intensity at 283 and 333 K.



Figure S4. Normalized phosphorescence spectrum of **Cou-Nap** in cyclohexane at 77 K. Note that the triplet energy (54.46 kcal/mol) was calculated from the 0–0 transition ($\lambda_{max} = 525$ nm) of phosphorescence spectrum.

Photolysis of Cou-Nap for [2+2] cycloaddition. As revealed from the X-ray determined molecular structure, the distance between two cofacially-oriented coumarin moieties in **Cou-Nap** is 3.8 Å. Thus, photoirradiation was anticipated to lead to intramolecular [2+2] cycloaddition. To inquire into this possibility, 0.1 M solution of **Cou-Nap** in CDCl₃ contained in an NMR tube was photolyzed in a Luzchem photoreactor fitted with 350 nm-UV lamps (14 lamps of 8 W power) under nitrogen gas atmosphere. Subsequently, the NMR spectra of the photolysate were recorded at different intervals of irradiation. As shown in Figure S5, the ¹H NMR signals of **Cou-Nap** were found to remain unchanged even after prolonged irradiation (for ca. 72 h) of the solution.



Figure S5. ¹H NMR (400 MHz) spectra of **Cou-Nap** (0.1 M in CDCl₃) recorded before (a) and after photoirradiation (350 nm) for 24 (b), 48 (c) and 72 h (d) under nitrogen gas atmosphere.



Figure S6. ¹H NMR (400 MHz, CDCl₃) spectra of 1.



Figure S7. ¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of 2.



Figure S8. ¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of Cou-Nap.



Figure S9. ¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of Cou-Dur.

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