

PHOTOPHYSICAL PROPERTIES OF FLUORENONES WITH CHIRAL SUBSTITUENTS AND THEIR ASYMMETRIC RECOGNITION THROUGH INTERMOLECULAR HYDROGEN BONDING INTERACTIONS IN THE EXCITED STATES

YOSHIHIDE AIKAWA, TETSUYA SHIMADA, HIROSHI TACHIBANA, AND HARUO INOUE*
Department of Applied Chemistry, Graduate Course of Engineering, Tokyo Metropolitan University
1-1, Minami-ohsawa, Hachiohji city, Tokyo, 192-0397 Japan

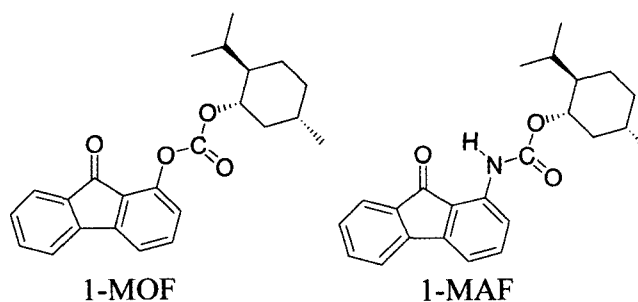
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Abstract—Asymmetric recognition of chiral alcohol by fluorenone derivatives with chiral substituents through intermolecular hydrogen bonding interaction in the singlet excited state was attempted. 1-((1S, 2R, 5S)-(+)-Menthylloxycarbonyl)aminofluoren-9-one (1-MAF) and 1-((1S, 2R, 5S)-(+)-menthylloxycarbonyl)oxyfluoren-9-one (1-MOF) were synthesized and their photophysical behaviors were characterized by the measurement of absorption and fluorescence spectra, as well as the quantum yield and the lifetime of fluorescence. The excited singlet states of 1-MAF and 1-MOF were revealed to have characteristics similar to those of fluorenone, though the intramolecular CT nature was fairly suppressed as compared with 3- and 4-substituted aminofluorenones. Fluorescences of 1-MAF and 1-MOF in acetonitrile were quenched by the addition of alcohols. Differences in fluorescence quenching efficiency were hardly observed for rather small chiral alcohols such as (R)-(-)- or (S)-(+)-2-butanol, while bulky alcohols such as menthol and isopinocampheol showed chiral recognition effects in their fluorescence quenching of 1-MAF in either acetonitrile or butyronitrile.

INTRODUCTION

Asymmetric chemistry in the electronically excited state has long attracted much attention.^{1,2)} Optical yields reported for the excited asymmetric chemistry, however, are generally not very high except in certain special cases.¹⁻³⁾ Intermolecular processes in the excited state involving asymmetric induction or molecular recognition are mostly governed by electron donating and accepting interactions.⁴⁻¹³⁾ Electron transfer interactions can operate at distances significantly longer than the molecular radius.¹⁴⁾ Full contact between the two molecules required for molecular recognition may not be attained in many cases. A more promising intermolecular interaction for asymmetric molecular recognition in the excited state would be one involving hydrogen bonding which can only operate at a distance less than 2 Å. Full contact between the two corresponding molecules is expected at this distance. Excited states of aromatic carbonyl compounds with electron donating substituents such as aminoanthraquinones and aminofluorenones have been revealed to have strong intermolecular hydrogen bonding interactions with alcohols.¹⁵⁻¹⁷⁾ The fluorescence of the aromatic carbonyls is efficiently quenched by the selective hydrogen bonding interaction

between the carbonyl oxygen and the hydroxyl hydrogen of the alcohols. Dual modes of highly anisotropic hydrogen bonding, both in-plane and out-of-plane relative to the fluorenone molecular plane, are involved in the fluorescence quenching.^{18,19)} Introduction of a chiral substituent in the 1-position of fluorenone would be expected to regulate the anisotropic intermolecular hydrogen bonding between the carbonyl oxygen and the hydroxyl hydrogen of the alcohols. As the first step towards asymmetric molecular recognition in the excited state, we report here syntheses of fluorenone derivatives with a chiral substituent in the 1-position, characterization of their photophysical behavior in the excited singlet states, and determination of their fluorescence quenching behavior affected by chiral alcohols.



Structural formula (1)

*To whom correspondence should be addressed.

MATERIALS AND METHODS

Syntheses of 1-substituted fluorenone derivatives. 1-((1S, 2R, 5S)-(+)-Menthylloxycarbonyl)aminofluorene-9-one(1-MAF): (1S)-(+)-Menthylchloroformate (2.3 mmol, 0.51 g) was added dropwise to a pyridine solution (20 mL) of 1-aminofluorenone (0.52 mmol, 0.1 g) and the mixture was refluxed for 30 min. After cooling the reaction mixture to room temperature, it was poured into water and evaporated. The obtained crude product was purified by column chromatography (SiO₂, eluent: benzene). Yield :99%. FAB-MS: *m/e* 378. ¹H NMR(δ /ppm) in C₆D₆: 0.58-1.01(12H, m), 1.22-1.48(4H, m), 2.04-2.10(2H, m), 4.90(1H, td), 6.60(1H, d), 6.70-6.73(1H, m), 6.91-7.02(3H, m), 7.43(1H,d), 8.56(1H, d),9.93(1H, s).

1-((1S, 2R, 5S)-(+)-Menthylloxycarbonyl)oxyfluorene-9-one(1-MOF): (1S)-(+)-Menthylchloroformate (2.0 mmol, 0.36g) was added to a pyridine solution (20mL) of 1-hydroxyfluorenone (1.1 mmol, 0.21 g) and the mixture was stirred for 5 min. The mixture was poured into water, extracted with diethylether, and evaporated. The crude product was purified by column chromatography (SiO₂, eluent: dichloromethane). Yield :80%. FAB-MS: *m/e* 379. ¹H NMR(δ /ppm) in DMSO-d₆: 0.81-9.93(10H, m), 1.03-1.19(2H, m), 1.43-1.48(2H, m), 1.66 (2H, d), 2.06(1H, td), 2.14(1H, d), 4.53(1H, td), 7.16(1H, d), 7.40(1H, t), 7.59-7.68(3H, m), 7.74(1H, d), 7.84(1H, d).

Measurements. The absorption spectra were measured with a Shimadzu UV-2100PC spectrophotometer. The steady-state fluorescence spectra were measured with a Hitachi F-4010 spectrofluorometer equipped with a Hamamatsu R928 photomultiplier tube. Instrumental response was adjusted using rhodamine B in ethylene glycol and a standard tungsten lamp. Fluorescence quantum yields (Φ_F) were determined by comparison with quinine bisulfate in 0.5 M aqueous sulfuric acid solu-

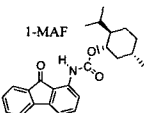
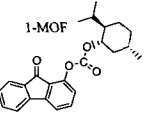

tion ($\Phi_F = 0.546$). Use of this value as a standard was verified by observing that of anthracene in ethanol ($\Phi_F = 0.28$). The literature value for anthracene is 0.27. A refractive index correction was made for each sample. The solutions were prepared with absorbances around 0.05 in order to avoid inner filter effect. The fluorescence decay and time-resolved fluorescence spectra were measured using a picosecond fluorescence lifetime measurement system under photon-counting conditions (a Hamamatsu C4334 streak scope, connected with a CHROMEX 250IS polychromator) with a Hamamatsu PLP-02 semiconductor laser (420 nm, 20 ps, 1.19 mW, 1 MHz) and EKSPLA PV-401 an optical parametric generator (420-560 nm, 25 ps, > 1 mJ, 5 Hz) pumped by the third harmonic radiation of a Nd³⁺ YAG laser, EKSPLA PL2143B (355 nm, 25 ps, 15 mJ) or by the third harmonic of the PL2143B itself. The laser flux was reduced with neutral density filters to avoid multiphoton absorption processes and nonlinear effects in the latter case. A single picosecond optical pulse of the PL2143B in the regenerative amplifier was extracted by an InGaAs photodiode (Hamamatsu G3476-05) and used as a pretrigger for the streak scope. This method turned out to be very useful for avoiding the trigger jitter problem of the streakscope, because no additional jitter owing to this pretrigger method was involved. Fluorescence time profiles were fitted by a convolution method.

RESULTS AND DISCUSSION

Photophysical properties of 1-MAF and 1-MOF.

Absorption and fluorescence spectra of 1-MAF and 1-MOF were measured in benzene, acetonitrile, ethanol, and ethanol-O-d. The λ_{\max} 's, quantum yield (Φ_F) and lifetime (τ) of flu-

Table 1. Photophysical properties of fluorenone derivatives

Energy donor	Solvent	Absorption		Fluorescence					
		λ_{\max} nm	λ_{\max} nm	Φ_F 10 ⁻²	τ ns	$\Delta\nu$ 10 ³ cm ⁻¹	E_{0-0} 10 ⁴ cm ⁻¹	k_r 10 ⁷ s ⁻¹	k_{nr} 10 ⁸ s ⁻¹
	Benzene	364	492	4.2	4.7	7.1	2.27	0.89	2.0
	Acetonitrile	363	504	4.9	8.9	7.7	2.25	1.1	2.2
	Ethanol	363	530	1.5	0.07/4.8	8.7	2.20	0.31	2.0
	Ethanol-O-d	379	528	2.1	0.07/6.7	8.6	2.21	0.31	1.5
	Benzene	379	479	0.49	1.7	5.5	2.31	0.10	2.1
	Acetonitrile	379	502	2.4	10	6.4	2.27	0.48	2.0
	Ethanol	376	537	0.55	0.06/4.4	8.0	2.22	0.12	2.3
	Ethanol-O-d	378	537	0.82	0.09/6.6	7.8	2.22	0.12	1.5
	Benzene	380	485	0.78	2.8	5.7	2.29	0.28	3.5
	Acetonitrile	377	514	2.3	19	7.1	2.24	0.12	0.52
	Ethanol	379	562	0.11	0.04/2.1	8.6	2.21	0.052	4.8
	Ethanol-O-d	--	--	0.16	0.05/4.0	--	--	0.040	2.5

Φ_F : Quantum yield of fluorescence, τ : Lifetime of fluorescence, E_{0-0} : Zero-zero level of S₁, $\Delta\nu$: Difference between wave-numbers at λ_{\max} 's of absorption and fluorescence, $k_r (= \Phi_F/\tau)$: radiative rate constant, $k_{nr} (= 1/\tau - k_r)$: Non-radiative rate constant.

orescence were measured in each solvent. The time resolved fluorescence in ethanol and ethanol-O-d exhibited biexponential decay. Since the shorter decay constants were thought to reflect the dielectric relaxation of ethanol, the longer ones were adopted as the lifetime. The zero-zero level of the lowest excited singlet state ($E_{0,0}$) was determined by the energy corresponding to the wavelength of the crossing point between the normalized absorption and the fluorescence spectra. The radiative rate constant (k_r) and the non-radiative one (k_{nr}) of the lowest excited singlet state (S_1) were calculated by eqs. 1 and 2.

$$k_r = \Phi_f F / \tau \quad (1)$$

$$k_{nr} = 1 / \tau - k_r \quad (2)$$

All of the obtained data on 1-MAF and 1-MOF are listed and compared with those of fluorenone in Table 1.

The λ_{max} 's of the fluorescence spectra of both 1-MAF and 1-MOF exhibited substantial red-shifting in polar solvents such as acetonitrile and ethanol as compared with those in benzene, while the absorption spectra remained almost unchanged. This tendency is quite similar to that of fluorenone. (Table 1) This indicates that the fluorescent states of these compounds are substantially stabilized in polar media. This tendency is evidently observed both in the difference between the wave numbers for absorption and fluorescence ($\Delta\nu$), and in the zero-zero levels of S_1 ($E_{0,0}$). The radiative rate constant, k_r , is a good measure of how the electronic state is influenced by the surrounding environment.¹⁵⁾ Both 1-MAF and 1-MOF have smaller k_r values in ethanol, though the value for 1-MOF in benzene is exceptionally small. This tendency is more evident in the case of fluorenone; the k_r is very small in ethanol. This strongly suggests that the electronic character of the fluorescent state is greatly affected by ethanol. The non-radiative rate constant, k_{nr} , also provides crucial information on the energy dissipation from the excited states. An appreciable deuterium isotope effect was observed among the k_{nr} values in ethanol and ethanol-O-d in all the cases of 1-MAF, 1-MOF, and fluorenone; $k_{nr}(\text{ethanol})/k_{nr}(\text{ethanol-O-d}) = 1.33$ (1-MAF), 1.53 (1-MOF), and 1.92 (fluorenone). This strongly suggests that the non-

radiative deactivation from S_1 is mainly caused by an intermolecular hydrogen bonding interaction between the carbonyl oxygen of fluorenone derivatives and the hydroxyl hydrogen of ethanol as demonstrated in aminofluorenones.¹⁹⁾ All of the observed photophysical data indicate that 1-MAF and 1-MOF have sufficiently polar excited states, intramolecular charge transfer states, as suggested by molecular orbital calculations, and the intermolecular hydrogen bond can cause the deactivation. The degrees of intramolecular charge transfer in their excited states, though, are less than those of aminofluorenone derivatives.¹⁶⁾ Since the fluorescence of fluorenone is known to be quenched by alcohol,²⁰⁻²²⁾ the excited states of 1-MAF and 1-MOF which have characteristics similar to those of fluorenone should be potential candidates for exhibiting molecular recognition by alcohol-type molecules.

Photophysical behavior of 1-MAF and 1-MOF in chiral alcohol.

The photophysical properties of 1-MAF and 1-MOF were further examined in chiral alcohol, (R)-(-)-2-butanol and (S)-(+)-2-butanol. Quantum yield (Φ_f), lifetime (τ) of fluorescence, difference between the wave numbers of absorption and fluorescence ($\Delta\nu$), zero-zero levels of S_1 ($E_{0,0}$), and radiative (k_r) and non-radiative (k_{nr}) rate constants in chiral 2-butanol are compared in Table 2.

The longer lifetimes in the two-component decay were used for the calculation of k_r and k_{nr} . Almost no difference is observed between the photophysical properties of 1-MOF in either R- or S-2-butanol, while the k_{nr} value of 1-MAF exhibits a small difference. This suggests a potential for chiral recognition by 1-MAF. As described later, PM3 molecular orbital calculations indicate that both in the ground and excited states of 1-MAF has a molecular configuration as in Fig. 1: (I) in the ground state or in Fig. 2: (I') in the excited state as the major species where the chiral menthyl substituent is situated on the opposite side from the carbonyl oxygen, while in the other metastable states (II, III, IV in the ground state or II', III', IV' in the excited state) the chiral group would regulate the approach of a third molecule

Table 2. Photophysical properties of fluorenone derivatives

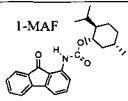
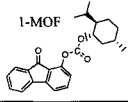
Energy donor	Solvent	Φ_f /10 ⁻²	τ /ns	$\Delta\nu$ /10 ³ cm ⁻¹	$E_{0,0}$ /10 ⁴ cm ⁻¹	k_r /10 ⁷ s ⁻¹	k_{nr} /10 ⁸ s ⁻¹
 1-MAF	(R)-(-)-2-Butanol	2.4	0.11/6.3	8.4	2.20	0.38	1.5
	(S)-(+)-2-Butanol	2.4	0.12/6.1	8.4	2.20	0.39	1.6
 1-MOF	(R)-(-)-2-Butanol	1.2	0.09/7.3	7.3	2.24	0.15	1.3
	(S)-(+)-2-Butanol	1.2	0.11/7.6	7.3	2.24	0.16	1.3

Table 3. Quenching of fluorescence of 1-MAF of bulky chiral alcohols.

T	Solvent	(1R, 2S, 5R)-(-)-Menthol		(1R, 2S, 5R)-(+)-Menthol		Ratio	(1R, 2R, 3R, 5S)-(-)-Isopinocampheol		(1R, 2R, 3R, 5S)-(+)-Isopinocampheol		Ratio
		K_{SV}	k_q	K_{SV}	k_q		K_{SV}	k_q	K_{SV}	k_q	
195	C ₃ H ₇ CN	3.47	-	2.05	-	1.7	-	-	-	-	-
280	CH ₃ CN	0.62	6.4	0.76	7.8	1.2	0.65	6.6	0.57	5.8	1.1
293	CH ₃ CN	0.32	3.6	0.35	4.0	1.1	0.41	4.7	0.36	4.1	1.1
313	CH ₃ CN	0.20	2.6	.021	2.7	1.0	0.23	3.0	0.22	2.9	1.0
328	CH ₃ CN	0.14	2.1	0.13	1.9	0.9	0.16	2.3	0.17	2.5	0.9

T/K, K_{SV}/M^{-1} , $k_q/10^7M^{-1}s^{-1}$, Ratio= $K_{SV}(\text{major})/K_{SV}(\text{minor})$

to the carbonyl oxygen. These calculations strongly encourage further experimental examination of chiral recognition by the excited 1-MAF. Molecular recognition of more bulky chiral alcohols such as menthol and isopinocampheol would be expected to be more easily accomplished.

Molecular Structure of 1-MAF estimated by Molecular Orbital Calculation.

PM3 molecular orbital calculations were carried out to esti-

mate the molecular structure of 1-MAF both in the ground and excited states. After getting an optimized molecular structure in both states, the heat of formation was calculated and its dependence on each dihedral angle of 1-2-3-4, 2-3-4-5, and 3-4-5-6 was compared as indicated in Figs. 1 and 2.

Among the three dihedral angles, the rotation of the N-C bond (3-4-5-6) from the optimized structure caused the largest destabilization, and thus the other two dihedral angles were chosen as the two coordinate axes for the consideration of the molecular configuration. In both the ground and

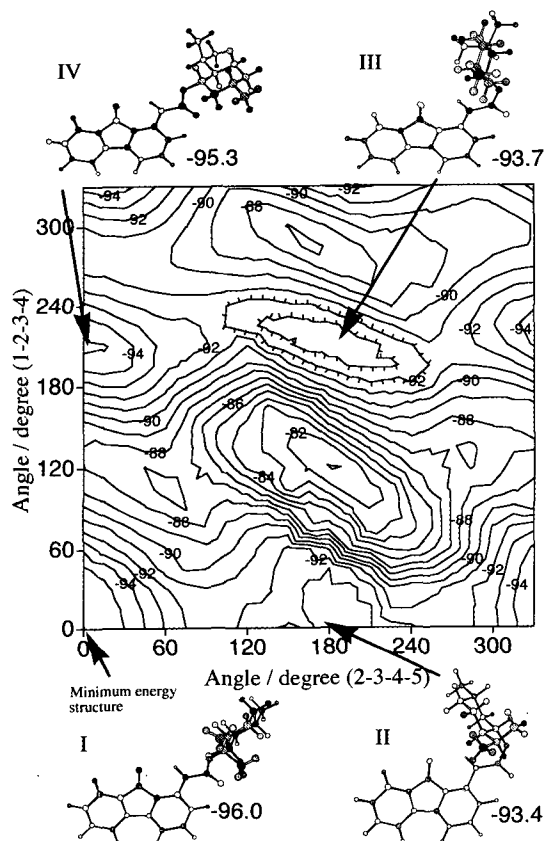


Fig. 1 Contour map of the heat of formation in the ground state of 1-MAF obtained by PM3 calculation: The numerals in the map denote the heat of formation in kcal/mol.

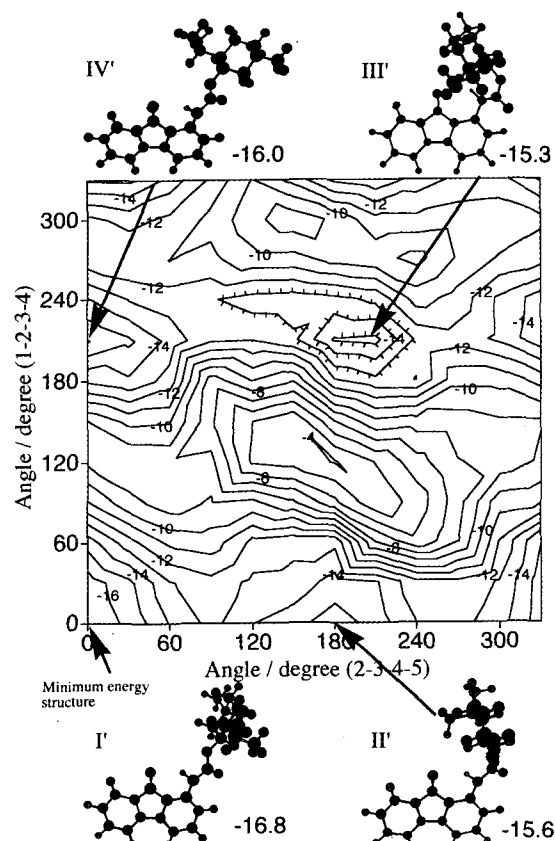
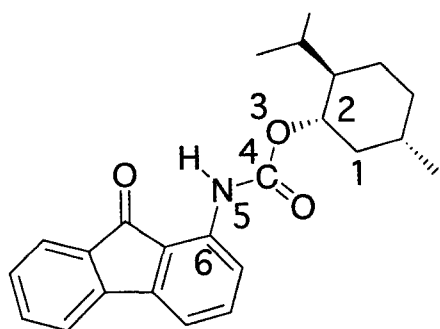


Fig. 2 Contour map of the heat of formation in the excited singlet state of 1-MAF obtained by PM3 calculation: The numerals in the map denote the heat of formation in kcal/mol.



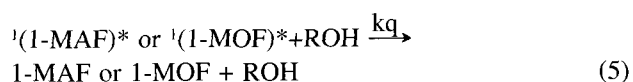
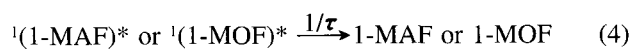
Definition of dihedral angle of 1-MAF

excited states, three other local minimum points were obtained in addition to the optimized molecular structure (I in the ground state and I' in the excited state) which were situated at the origin of the coordinate axes. In the three molecular structures, the chiral menthyl group is getting closer to the carbonyl group than it is in the optimized structure (I or I'). This tendency is more evident in the excited state. One would expect the three metastable structures II', III', IV' in the excited state would be expected to well-regulate the approach of a third molecule to the carbonyl group.

Fluorescence quenching by bulky chiral alcohols.

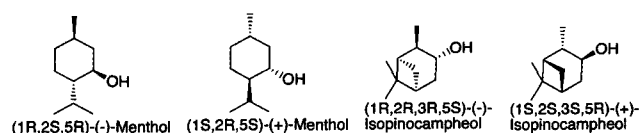
Fluorescences of 1-MAF and 1-MOF were measured in acetonitrile. When ethanol was added to the acetonitrile solution of 1-MAF or 1-MOF, the fluorescence intensity of the fluorenones was decreased in accord with the Stern-Volmer relation in equation (3). The fluorescence quenching is characterized by eqs. (4), (5). The quenching rate constant k_q was calculated from K_{SV} and lifetime τ ; $k_q = 3.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (1-MAF), $2.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (1-MOF). The rate constants are very similar to that reported for fluorenone ($7.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$).²⁰⁾

$$I_F^0 / I_F = 1 + k_q \tau [\text{ROH}] = 1 + K_{SV} [\text{ROH}] \quad (3)$$



(1R, 2S, 5R)-(-)-Menthol, (1S, 2R, 5S)-(+)-menthol, (1R, 2R, 3R, 5S)-(-)-isopinocampheol, and (1S, 2S, 3S, 5R)-(+)-isopinocampheol also quenched the fluorescence of 1-MAF or 1-MOF in acetonitrile.

The quenching rate constants k_q were on a similar order with those of ethanol as described above. As observed in 2-butanol, 1-MOF did not suffer any difference in the fluorescence quenching by the chiral alcohols: $K_{SV}=1.2$ ((-)-menthol), 1.2 ((+)-menthol), 1.2 ((-)-isopinocampheol), 1.2 ((+)-



Structural formula (2)

isopinocampheol) at 293K, 1-MAF showed more interesting results as summarized in Table 3. Both menthol and isopinocampheol showed evident differences among the chiral isomers in the fluorescence quenching of 1-MAF. The quenching process was confirmed to be strictly dynamic by observing the Stern-Volmer relationship in lifetime measurements at 280 and 293 K. Table 3 obviously indicates that temperature greatly affects the chiral recognition; a lower temperature favors quenching by (-)-menthol and (-)-isopinocampheol. Owing to the freezing point limitation (fp of $\text{CH}_3\text{CN}=228 \text{ K}$), the fluorescence quenching was further examined at lower temperature in butyronitrile (fp=161.1 K). At 195 K a fairly high recognition was observed for menthol as expected: $K_{SV}((-)\text{-menthol}) / K_{SV}(+)\text{-menthol} = 1.7$. Though these results are still preliminary, they are very suggestive of a strategy that could lead to higher molecular recognition. Even though the molecular structures of the chiral fluorenones, in both the ground and excited states, are mostly unfavorable for chiral recognition, appreciable differences in the chiral recognition were observed as summarized in Table 3. Better-designed chiral fluorenones could possibly exhibit higher molecular recognition.

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