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Luminescence properties of novel soluble quinacridones

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Abstract

Some 5,12-*N*,*N*′-dialkyl-2,9-dialkyloxy quinacridones were synthesized. These compounds have good solubility in organic solvents such as dichloromethane, chloroform, acetone, ethyl acetate and their spectral properties were also investigated. The comparison of absorption spectra and fluorescence spectra of these soluble quinacridones between in solutions and in solid film indicated that the formation of intermolecular hydrogen bonds in the crystalline was obstructed by *N*-alkylation. The fluorescence lifetime of the soluble quinacridone was measured by single-photon counting technique. The longer fluorescence lifetime (ca. 20 ns) of the compound seems to be hopeful for the luminescence application.

Keywords: Soluble quinacridones; Synthesis; Luminescence properties

1. Introduction

Linear *trans*-quinacridones (QA) [1] are widely used organic pigment for the applications of high-sensitivity photosensors or photoreceptors required for electro-photography [2], solar cells [3,4], organic light-emitting diodes (LED) [5,6] and optical probes, etc [7,8]. They have the broad absorption region (400–600 nm) and exhibit excellent fastness properties. Meanwhile, quinacridones have also strong emission property in the solid film. Therefore, QA was used often as a fluorescent guest in organic LED [9,10]. However, the quinacridone derivatives can easily form an excimer by the hydrogen bond. In general, the excimer and exciplex may result in quenching or a non-radiative pathway. The inferior stability of the QA doped EL device would lead one to believe that the tendency for intermolecular hydrogen bonding between QA molecules is the driving force for the formation of non-radiative centers, which are responsible for the loss of EL efficiency in operation [9]. These non-radiative centers may be dimeric QA or other degradation products from a QA precursor. The formation of such dimer molecules may gradually degrade the EL efficiency during operation because the dimer molecule is generally non-fluorescent and therefore provides a new non-radiative pathway for the dissipation of the EL excitation energy. Hence, it is highly desirable to produce a variant of quinacridone structure that will provide the organic EL device with enhanced efficiency and stability. Shi and Tang [9] designed and used *N*,*N*′-dimethyl-substituted QA (DMQA) for the dopant in EL device. The improved stability of EL device observed (half-life about 7500 h) was attributed to the elimination of intermolecular hydrogen bonding between the dopant molecules. However, it had been also observed that the EL efficiency decreased and the EL spectra were slightly red-shifted and broadened with increasing DMQA concentration [9]. These observations can be generally attributed to the formation of dimers and higher oligmers of DMQA molecules in the AlQ_3 host. This means that *N*,*N*′-DMQA did not form an uniform phase with the host material when the concentration of DMQA was higher than 1.8 wt.% in the host. The further modification in the structure for substituted QA is necessary in order to obstruct completely the formation of dimeric QA or other degradation products from a QA precursor.

The intermolecular hydrogen bonds in *trans*-quinacridones are believed to contribute considerably to the high thermal, chemical and photochemical stability. The chemical resistance of QA molecules owing to hydrogen bonds is desirable for pigment use with reference to climate immunity, but is not desirable for LED use. On the other hand, the insolubility of *trans*-quinacridones limits also their applications sometime. For example, preferred fluorescent materials for the application of EL are in generally those which form a common phase with the host material. One approach is improvement on the solubility of fluorescence materials. In the case of the non-substituted QA, the N–H moiety

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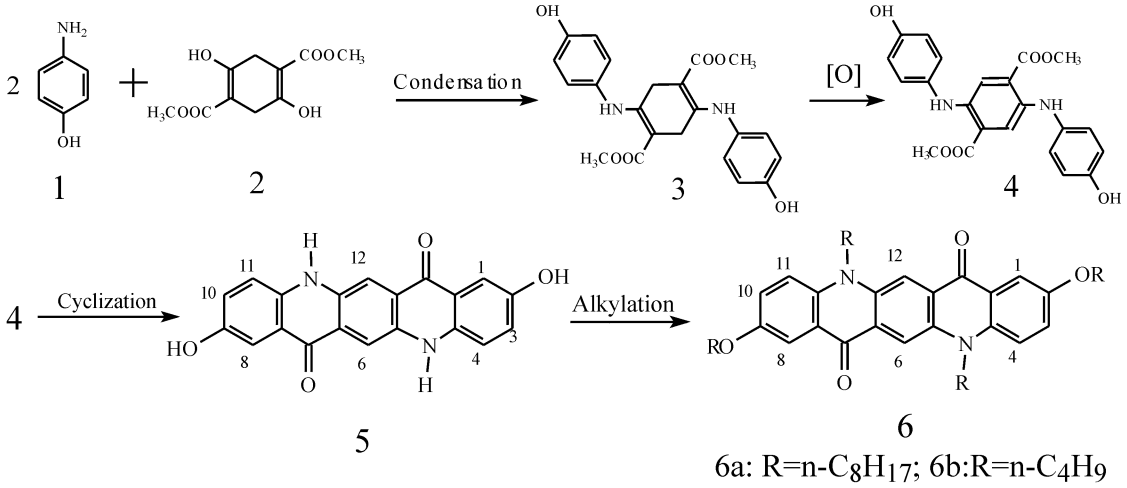

Scheme 1. The synthesis route of tetra-substituted quinacridones.

permits intermolecular hydrogen bonding between neighboring QA molecule [11], favored by the planar geometry of the molecule. Thus, it is anticipated that a modification of QA structure is necessary to provide for EL operation, both improved efficiency and stability. Multi-substitution of quinacridones could improve the solubility [11–13]. For examples, 5,12-di(*N*-alkylation) quinacridones have an improved solubility due that the formation of intermolecular hydrogen bonds was obstructed by *N*-alkylation. Since an introduction of *n*-dodecyloxy groups in the 2- and 9-position of quinacridone did not result in an improved solubility, as reported similarly for 2,9-di(alkyl) quinacridone [14], we synthesized substituted title quinacridones with 2,9-dialkyloxy substitution and *N*-alkylation (i.e. 5,12-dialkyl) shown in Scheme 1. These substituted quinacridones have an obvious improved solubility in most of organic solvents such as dichloromethane, chloroform, acetone, ethyl acetate, etc. In the *N*-alkyl-substituted QA, the interaction between molecules is completely blocked due to the *N*-alkylation. Thus their spectral properties in solutions and in solid film were investigated. The fluorescence lifetime of the soluble quinacridone was measured by single-photon counting technique. The compound has a longer fluorescence lifetime (ca. 20 ns). These compounds are expected to meet some specified requirements.

2. Experimental

^{1}H NMR spectroscopy: Bruker AVNNCE 500 MHz (relative to TMS). Mass spectroscopy: L6 FAB or America MA1212. Infrared spectroscopy: Shimadzu IR-408. UV–Vis spectroscopy: Shimadzu UV-260. Fluorescence spectroscopy: HITACHI-850. Melting points: X4 micro-melting point apparatus. Fluorescence lifetimes of compounds were measured by single-photon counting technique (Edinburgh FL 900) with a hydrogen-filled flash lamp or a nitrogen lamp as the excitation source. Data were analyzed using a non-linear least-squares fitting program with deconvolution method. The temporal resolution after deconvolution of the exciting pulse is ∼200 ps.

2.1. Dimethyl 2,5-bis(p-hydroxyanilino)-3,6-dihydro terephthalate (3)

A mixture of 7.12 g (65.2 mmol) of *p*-aminophenol, fresh hydrochloric acid 3.2 ml, *N*-methyl-2-pyrrolidone (NMP) 25 ml was heated. After dissolved, 5 g (21.9 mmol) of dimethylsuccinylosuccinate was added to the solution. The reaction was carried out under argon at 120°C for 3 h (TLC was used for the determination of reaction process). After cooling to room temperature, the mixture was poured under stirring into 250 ml of water. The precipitated product was filtered, washed with water, and dried in vacuum and with P_2O_5. Purification by chromatography (silicon gel column, ethyl acetate: petroleum ether = 1:3) afforded 7.73 g of pure compound **3** as a pale yellow powder with a yield of 86.1%. M.p.: 237–239°C. IR (KBr): ν = 3370 cm^{-1} (O–H), 3262 cm^{-1} (N–H), 2980–2850 cm^{-1} (C–H), 1684,1300 cm^{-1} (C(O)–O), 1520 cm^{-1} (C=C); ^{1}H NMR (DMSO-d_6): 3.24 (s, 4H, allylic C–H in cyclohexadiene ring) 3.64 (s, 6H, –$COOCH_3$), 6.77 (d, 4H, J = 8.24 Hz, hydroxyl *m*-protons), 7.02 (d, 4H, J = 8.51 Hz, hydroxyl ortho protons), 9.53 (s, 2H, –NH–), 10.29 (s, 2H, –OH); MS: *m*/*z* (rel. intensity): 316 (M^+–Ph–OH, 100%), 284 (63), 253 (23), 225 (71); FAB-MS: *m*/*z* 411 $(M+1)^+$.

*2.2. Dimethyl 2,5-bis(p-hydroxyanilino)-terephthalate (**4**)*

Five grams (12.2 mmol) of compound **3** was dissolved in 20 ml of NMP. Then 0.78 g (24.33 mmol) of sulfur was added. The reaction was carried out in an argon atmosphere at 115°C for 2 h till no H_2S gas giving out (TLC was used for the determination of reaction process). After cooling

to room temperature, the mixture was poured into 200 ml of water. The precipitated product was filtered, washed with water, and dried in vacuum and with P_2O_5. Purification by chromatography (silicon gel column, ethyl acetate: petroleum ether = 1:2) afforded 3.73 g of pure compound **4** as a bright red powder with a yield of 75%. M.p.: 263–265°C. IR (KBr): Broad band 3500–3100 peaking at 3380 cm^{-1}, 2955–2850 cm^{-1} (C–H), 1675, 1220 cm^{-1} (C(O)–O); ^{1}H NMR (DMSO-d_6): 3.76 (s, 6H, –$COOCH_3$), 6.75 (d, 4H, J = 8.61 Hz, hydroxyl *m*-protons), 6.98 (d, 4H, J = 8.62 Hz, hydroxyl ortho protons), 7.49 (s, 2H, central ring C–H), 8.24 (s, 2H, –NH–) 9.27 (s, 2H, –OH); MS: *m*/*z* (rel. intensity): 408 (M^+, 100%); absorption peaks (in DMSO) λ^{Ab} (nm) ($\log \varepsilon$): 309.6 (4.29), 493.6 (3.72); fluorescence peaks λ_{em}^{max} (in DMSO, excited: 309.6 nm) = 342.1 nm.

2.3. 2,9-Dihydroxy quinacridone (**5**)

A three-neck round-bottom flask was charged with 20 ml of poly phosphoric acid (PPA), heated to 80°C. Then 3 g (7.34 mmol) of **4** was added. Air was thoroughly removed from the slurry and the apparatus by repeated evacuation/argon-flushing cycles. The mixture was heated to 165°C for 1 h. After cooling to 70°C, 20 ml of ethanol was added, stirred for 1 h. Then cooling to room temperature, the mixture was poured into 200 ml of water, centrifuged, washed with water till neutralization. The solid residue was soxhleted with acetone to give 2.1 g of compound **5** as a purple powder. M.p. > 300°C. IR (KBr): broad band 3620–2000 peaking at 3220 with detail at 3250, 2370, 1602 cm^{-1} (C=O); FAB-MS: *m*/*z* 345$(M+1)^+$. Absorption peaks (in DMSO) λ^{Ab} (nm) ($\log \varepsilon$): 300.4 (5.15), 503.0 (3.94), 536.2 (4.08). Fluorescence peaks λ_{em}^{max} (in DMSO, excited: 300.4 nm) = 555.1 nm.

2.4. 5,12-Dioctyl-2,9-dioctyloxy quinacridone (**6a**)

One gram of compound **5**, 100 ml toluene, 0.9 g (2.79 mmol) of tetrabutylammonium bromide (TBAB) and 37.5% aqueous potassium hydroxide (40 g) were vigorously stirred and heated to reflux. When **5** had completely dissolved, 25 ml (0.14 mmol) of 1-octyl bromide was added, stirred vigorously for 12 h. The residue was purified by chromatography (silicon gel column, CH_2Cl_2: petroleum ether = 5:1) to afford 0.55 g of the title compound **6a** as a red powder. M.p.: 162–164°C. IR (KBr): ν = 2950, 2920, 2850 cm^{-1} (C–H), 1290, 1275 cm^{-1} (C–O–C), 1615 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): 0.90 (m, 12H, $4CH_3$), 1.25–1.66 (m, 48H, $24CH_2$), 1.86–2.01 (m, 8H, $4CH_2$), 4.13 (t, 4H, –NCH_2–), 4.56 (t, 4H, –OCH_2–), 7.45 (dd, 2H, J = 9.36, 2.88 Hz, $C_{3,10}$–H), 7.53 (d, 2H, J = 9.36 Hz, $C_{4,11}$–H), 7.98 (d, 2H, J = 2.88 Hz, $C_{1,8}$–H), 8.83 (s, 2H, central ring C–H); MS: *m*/*z* (rel. intensity): 149 (100%), 167 (10.6%), 70 (20%); FAB-MS: *m*/*z* 793$(M+1)^+$. Absorption peaks (in CH_2Cl_2) λ^{Ab} (nm) ($\log \varepsilon$): 309.8 (5.05), 512.0 (3.76), 549.6 (4.02); fluorescence peaks λ_{em}^{max} (in CH_2Cl_2, excited: 309.8 and 350 nm) = 568.7 nm.

2.5. 5,12-Dibutyl-2,9-dibutyloxy quinacridone (**6b**)

The synthetic procedures were similar to **6a** except that the 1-butyl bromide was used instead of 1-octyl bromide. Purification by chromatography (silicon gel column, ethyl acetate: CH_2Cl_2 = 1:40) to afford 0.46 g of the title compound **6b** as a red powder. M.p.: 192–194°C. IR (KBr): ν = 2960, 2930, 2870 cm^{-1} (C–H), 1285, 1260 cm^{-1} (C–O–C),1620 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): 0.99 (m, 12H, $4CH_3$), 1.40–1.54 (m, 16H, $8CH_2$), 1.85–2.04 (m, 8H, $4CH_2$), 4.13 (t, 4H, –NCH_2–), 4.54 (t, 4H, –OCH_2–), 7.42 (dd, 2H, J = 940, 2.97 Hz, $C_{3,10}$–H), 7.51 (d, 2H, J = 9.40 Hz, $C_{4,11}$–H), 7.97 (d, 2H, J = 2.97 Hz, $C_{1,8}$–H), 8.80 (s, 2H, central ring C–H); MS: *m*/*z* (rel. intensity): 162 (100%), 164 (34.2%), 135 (24%), 127 (30%); FAB-MS: *m*/*z* 569$(M+1)^+$; absorption peaks (in CH_2Cl_2) λ (nm) ($\log \varepsilon$): 304.0 (4.85), 500.0 (3.70), 537.6 (3.90); fluorescence peaks λ_{em}^{max} (in CH_2Cl_2, excited: 304.0 nm) = 560.9 nm.

3. Results and discussion

The absorption spectra data of the compounds studied in this work were listed in Table 1. As seen in Figs. 1 and 2, the shapes of the absorption spectra of compounds **5**, **6a** and **6b** are similar with each other. They have large absorption coefficients in the UV region. Comparing **5** with **6b**, the maximum absorption wavelength of compound **6a** is 549.6 nm, which is much longer than that of compound **5** and **6b**. This indicates that longer carbon chain substitution affects obviously the absorption of the substituted QA. The absorption data of compound **6a** in different solvents were listed in Table 2. The solvent effect, i.e. the maximum absorption wavelength shifts to longer wavelength region with increasing polarity of solvents, was not observed for compound **6a**.

Table 1
Absorption and solubility data of the compounds in solvents (10^{-5} mol/l)

Compounds (solvent)	Absorption peaks (nm) ($\log \varepsilon$)	Solubility (g/l)
4 (DMSO)	309.6 (4.29), 493.6 (3.72)	
5 (DMSO)	300.4 (5.15), 503.0 (3.94), 536.2 (4.08)	~1
6a (CH_2Cl_2)	309.8 (5.05), 512.0 (3.76), 549.6 (4.02)	Up to 40
6b (CH_2Cl_2)	304.0 (4.85), 500.0 (3.70), 537.6 (3.90)	Up to 30

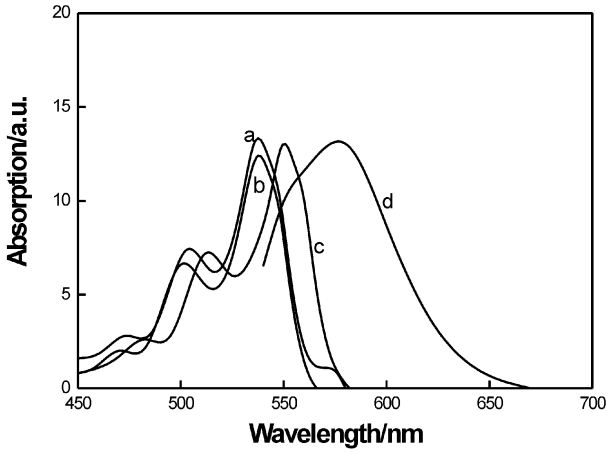

Fig. 1. Absorption spectra of **5** in DMSO (a); and in PC film (d); **6a** in CH_2Cl_2 (c); **6b** in CH_2Cl_2 (b).

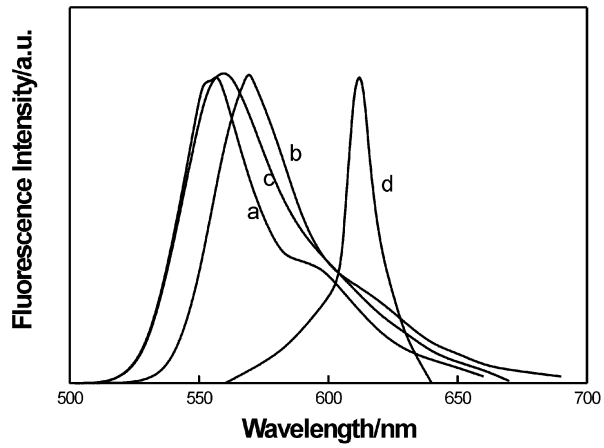

Fig. 2. Fluorescence emission spectra of compound **5** in DMSO (a); **6a** in CH_2Cl_2 (b); compound **6b** in CH_2Cl_2 (c); compound **5** in PC film (d).

This means that the interaction between molecules is completely blocked for compound **6a** due to the *N*-alkylation and 2,9-dialkyloxy substitution with longer carbon chain.

The dependence of the absorption on the concentration for compounds **5**, **6a** and **6b** were listed in Tables 3 and 4. The concentration-dependence of the absorption are observed for the non-substituted quinacridone [12,14,15] and compound **5**. The maximum absorption wavelength difference between in solutions and in solid film for compound **5** are large. This indicates that the intermolecular interaction between N–H and CO groups is very strong for compound **5** in the solid film, which was fabricated directly with the DMF solution (10^{-5} M) of compound **5** in polymer PC matrix under vacuum dry. The solid films of **6a** and **6b** were also fabricated by the same way with their CH_2Cl_2 solution (10^{-3} M). Unfortunately, the thickness ($\sim$10 μm) of the film was not exactly measured. This behavior is very similar with that of non-substituted QA in solid film. The intermolecular hydrogen bond will result in the formation of dimers or oligmers for compound **5**, whose maximum absorption wavelength shifts to red region about 44.4 nm, comparing with that of molecules. When dissolved in the high polar solvent concentrated sulfuric acid, compound **5** exhibits the characteristic spectrum of the quinacridone molecule with its long wavelength maximum at $\lambda = 600$ nm, which is still found at concentrations near 10^{-3} mol/l. Müllen and coworkers [13] reported the maximum absorption wavelength of 6,12-dihydro-2,3,9,10-tetra (dodecyloxy) QA in THF $\lambda = 502$ nm when the concentration was below than 10^{-4} mol/l. The more concentrated solutions exhibit additional, red-shifted absorption band at $\lambda = 558$ nm, which completely dominates the visible part of the spectrum for concentrations near 10^{-3} mol/l. When dissolved in low polar solvents such as CCl_4 or toluene, the quinacridone forms much more stable aggregates that are indicated by the characteristic aggregate absorption at 560 nm even at concentrations below 10^{-6} mol/l. The concentration-dependencies of the absorption are not observed for compound **6a**, whose difference of maximum absorption wavelength between in solutions and in solid film is relatively smaller. This indicates that the intermolecular hydrogen bonds are obstructed due to the 2,9-dialkyloxy substitution and *N*-alkylation (i.e. 5,12-dialkyl). The dimers

Table 2
The absorption spectra data of compound **6a** in different solvents

	Solvents				
	Petroleum ether	Ethyl acetate	Acetone	CH_2Cl_2	$CHCl_3$
λ_{max} (nm) ($\log \varepsilon$)	528.4 (4.07)	539.0 (4.15)	543.2 (4.05)	549.6 (4.12)	551

Table 3
Absorption data for quinacridone and some substituted derivatives

	λ^{Ab} max (nm)
Non-substituted QA [16]	519 (DMF), 557 (solid state), 597 (concentrated H_2SO_4)
5	536.2 (DMSO), 580.6 (in PC film), 600 (concentrated H_2SO_4)
6a	549.6 (CH_2Cl_2), 551.4 (in PC film)

Table 4
The concentration effect on the absorption of compound **5**, **6a** (λ max (nm) (log ε))

	Concentration (mol/l)			
	10^{-6}	10^{-5}	10^{-4}	10^{-3}
5 (concentrated H_2SO_4)	601.8 (3.70)	600.6 (3.66)	600.4 (3.75)	599.8 (3.65)
6a (CH_2Cl_2)	549.8 (4.02)	549.6 (4.02)	549.2 (4.02)	549.1 (4.02)

or oligmers of compound **6a** are not formed. The maximum absorption wavelength (549 nm) did not shift to red with increasing concentration. The improved solubility of **6a** and **6b** was quantitatively shown in Table 1.

The fluorescence lifetime data of compound **6a** in different solvents were listed in Table 5. The fluorescence emission decay according to single exponential kinetics. The lifetimes of compound **6a** detected at 620 nm were relatively longer (ca. 20 ns). For a guest–host EL system, guest molecules travel in the host matrix during the operation, and then the guest molecule forms the excimer with another guest molecule or the exciplex with the host molecule. The excimer and exciplex may result in the reduction of EL efficiency. For the tetra-substituted title quinacridone with 2,9-dialkyloxy substitution and *N*-alkylation (i.e. 5,12-dialkyl) synthesized in this work, the obstruction of the intermolecular hydrogen bond was confirmed by means of not only spectral properties shown in above but also the longer fluorescence lifetime. In general, the formation of excimer or exciplex would quench fluorescence and shorten the fluorescence lifetime. The longer fluorescence lifetime of compound **6a** indicates that non-radiative pathways, which would quench fluorescence, are not formed during light excitation. This results in higher fluorescence quantum yield, which was shown in Table 6. The tetra-substituted title quinacridone (**6a** and **6b**) with 2,9-dialkyloxy substitution and *N*-alkylation (i.e. 5,12-dialkyl) have relative higher fluorescence quantum yield, which is proportional to the fluorescence integrated area. Because that non-substituted QA was insoluble in common organic solvents, we cannot compare fluorescence intensity of **6a** and **6b** with non-substituted QA. As the same reasons, the molecular fluorescence lifetime of non-substituted QA in solution was never reported in literatures. Despite that the excitation for EL device differs from that of photoluminescence, the longer photoluminescence lifetime should be favorable for the enhancements of EL luminescence efficiency and the device stability. On the other hand, the longer fluorescence lifetime of **6a** implies that there exist the internal transition of excited singlet energy within the molecule. The fluorescence lifetime of **6a** did not depend on the polarity of the solvents. The longer fluorescence lifetimes may be the characteristic of the tetra-substituted QA molecules. This restriction of excited singlet energy in tetra-substituted QA molecules with 2,9-dialkyloxy substitution and *N*-alkylation should be utilized when designing new luminescence materials. This kind of tetra-substituted QA molecular structures could be used as effective (may be both for the enhancements in EL efficiency and stability) emitter segment in luminescence polymers. Work in this direction is in progress.

Table 5
The fluorescence lifetime data (excited at 350 nm, emission detected at 620 nm) of compound **6a** in different solvents (concentration indicated by the absorbance at 350 nm)

	Solvents (absorbance at 350 nm)		
	$CHCl_3$ (0.186)	Ethyl acetate (0.209)	CH_2Cl_2 (0.231)
τ (ns)	20.7	18.5	21.5

Table 6
Fluorescence data of the compounds in the solutions (10^{-5} mol/l) and in PC film

Compound (solvent)	λ_{ex} (nm)	λ_{max}^{Fl} (nm)	Fluorescence integrate ratio[a]
4 (DMSO)	309.6	342.1	
5 (DMSO)	300.4	555.1	1
6a (CH_2Cl_2)	309.8; 350	568.7	1.39
6b (CH_2Cl_2)	304.0	560.9	1.28
Non-substituted QA (solid film) [17]	436	678	
5 (in PC film)	305.8	612.0	
6a (in PC film)	535.5	595.4	

[a] The values are obtained by integrated area (integrated from 500 to 700 nm) ratio relative to that of **5**.

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