Luminescence

DOI: 10.1002/ange.200502214

Banana-Shaped Oligo(aryleneethynylene)s: Synthesis and Light-Emitting Characteristics**

Yoshihiro Yamaguchi, Shigeya Kobayashi, Tateaki Wakamiya, Yoshio Matsubara, and Zen-ichi Yoshida**

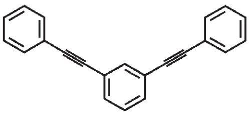
Bent (so-called banana-shaped) molecules which consist, for example, of an aromatic unit and ester unit are currently attracting interest in the field of liquid crystals.[1] However, to the best of our knowledge, the light-emitting efficiency of banana-shaped molecules have not been reported so far, even though bent light emitters have been reported.[2] In view of the growing importance of highly efficient light-emitting materials in biological, chemical, and materials science, we report here the synthesis and light-emitting characteristics of banana-shaped oligo(arylene ethynylene)s **2**–**6** containing pyridine rings as it is not clear what influence pyridine ring(s) would have on the emission characteristics.

In regard to the banana-shaped molecules, we considered **1** (the simplest trimeric hydrocarbon system), **2** (with a pyridine ring substituting the central benzene ring of **1**), **3** (with a pyridine ring substituting both terminal benzene rings of **1**), **4** (a donor/acceptor (OMe group/pyridine C=N group) trimeric system), **5** (donor/acceptor pentameric system with a single banana structure), and **6** (a donor/acceptor pentameric system with a double banana structure).

The synthesis of **4**–**6** was achieved by using the Sonogashira C–C coupling reaction[3] as the key step (Scheme 1). Although **1**,[4] **2**,[5] and **3**[6] are known compounds, we prepared them in a similar manner to **4**, that is, in a different way from the reported methods.[4–6] The structures of **1**–**6** were confirmed by spectral data (^{1}H and ^{13}C NMR spectroscopy and HR-FAB MS, see the Supporting Information).

The emission and absorption characteristics of **1**–**6** and the rod-shaped donor/acceptor pentameric systems (**15** and **16**)[7] together with the radiative rate constants (k_r), radiationless rate constants (k_d), $k_\mathrm{r}/k_\mathrm{d}$ (our measure for emissivity), and emission life times (τ) are shown in Table 1. Since the k_r and k_d values are related to the corresponding emission quantum yields and life times by $\Phi_\mathrm{f} = k_\mathrm{r}\tau$ and $k_\mathrm{r} + k_\mathrm{d} = \tau^{-1}$, it is possible to calculate the values of k_r and k_d whenever quantum yield and life time data are available.[8]

The important results contained in Table 1 are as follows: First, the Φ_f and $k_\mathrm{r}/k_\mathrm{d}$ values for **1**–**3** demonstrate that the emission efficiency markedly increases when the central pyridine ring is present (Φ_f: 0.48, $k_\mathrm{r}/k_\mathrm{d}$: 0.92 for **2**), while it greatly decreases when terminal pyridine rings are present (Φ_f: 0.03, $k_\mathrm{r}/k_\mathrm{d}$: 0.03 for **3**). Second, the introduction of MeO groups into both benzene rings of **2** (construction of the donor/acceptor system) leads to a more efficient light emitter (Φ_f: 0.58, $k_\mathrm{r}/k_\mathrm{d}$: 1.38 for **4**) than **2**. The maximum emission of **4** (λ_em: 397 nm) appears at a longer wavelength (by 49 nm) than that of **2** (λ_em: 348 nm). Third, and the most remarkable finding, is that the donor/acceptor pentameric system shown in single banana structure **5** is a highly efficient violet-light emitter (Φ_f: 0.84, λ_em: 414 nm, $k_\mathrm{r}/k_\mathrm{d}$: 5.25), and the donor/acceptor pentameric system shown in double banana structure **6** is an excellent violet-light emitter (Φ_f: 0.91, λ_em: 417 nm, $k_\mathrm{r}/k_\mathrm{d}$: 10.11) despite the interruption of the π conjugation by one *meta* substitution in the former and by two *meta* substitutions in the latter. It is evident that the Φ_f values for **5** and **6** are greater than those of the rod-shaped donor/acceptor pentameric systems **15** (Φ_f: 0.75, $k_\mathrm{r}/k_\mathrm{d}$: 3.00) and **16** ($\Phi_\mathrm{f}$: 0.76, $k_\mathrm{r}/k_\mathrm{d}$: 3.17).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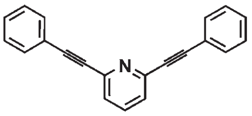
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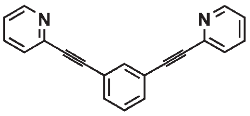
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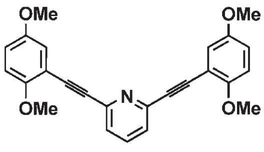
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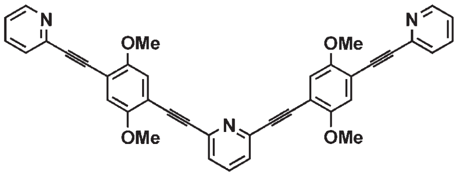
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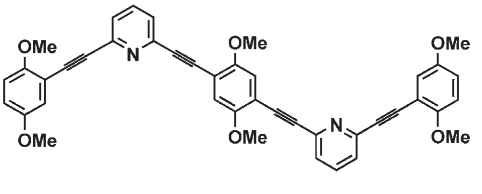
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The superior emissive properties of **5** and **6** (in particular of **6**) relative to **15** and **16** is ascribed to the decrease in their k_d values compared to those of **15** and **16**, since the k_r values of **5** and **6** are similar to those of **15** and **16**. It is well known that *meta*-substituted systems are weaker light emitters than the corresponding *para* isomers, as exemplified by bis(phe-

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[*] Prof. Dr. Y. Yamaguchi, Dr. S. Kobayashi, Prof. Dr. T. Wakamiya, Prof. Dr. Y. Matsubara, Prof. Dr. Z.-i. Yoshida
Faculty of Science and Engineering
Kinki University
Higashi-Osaka, Osaka 577-8502 (Japan)
Fax: (+81) 6-6723-2721
E-mail: yamaguch@chem.kindai.ac.jp
yoshida@chem.kindai.ac.jp

[**] We thank Professor Masanori Morita (Kinki University) for MS measurements and Yoko Maeda for assistance in this study. This work was supported by a Grant-in-Aid for Creative Scientific Research (No. 16GS0209) and Scientific Research (No. 16550131) from the Ministry of Education, Science, Sports, and Culture of Japan.

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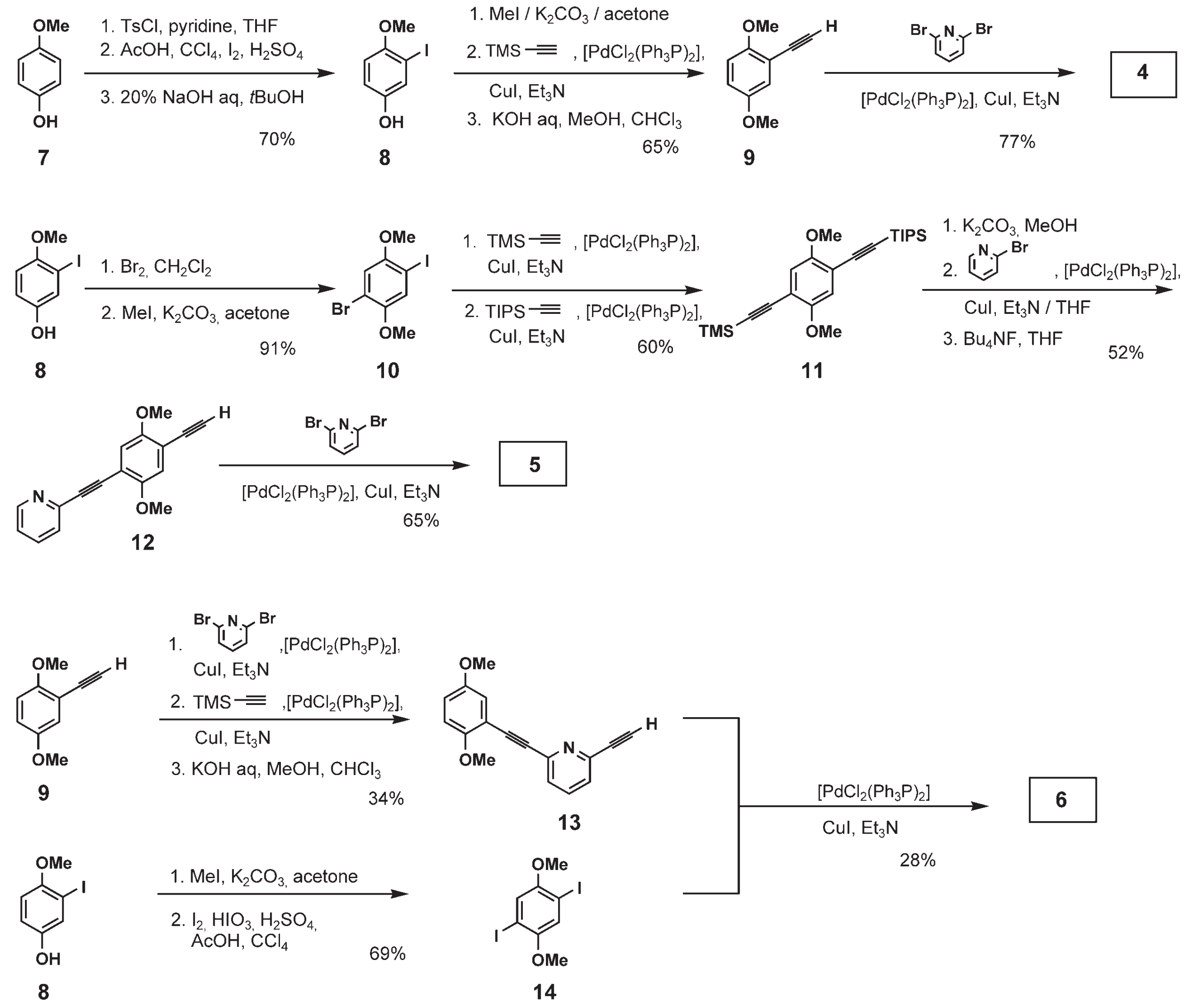
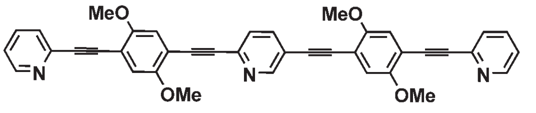


Scheme 1. Synthesis of donor/acceptor banana-shaped oligo(aryleneethynylene)s **4**, **5**, and **6**. Ts = toluene-4-sulfonyl, TMS = trimethylsilyl, TIPS = triisopropylsilyl.

Table 1: Emission and absorption characteristics of banana-shaped oligo(aryleneethynylene)s **1**–**6**, **15**, and **16** in CHCl$_3$.[a]

Compound	Φ_f[b]	λ_{em}[nm]	logε	λ_{abs}[nm]	τ[ns]	k_r[s^{-1}]	k_d[s^{-1}]	k_r/k_d
1	0.14	330	4.70	302	2.00	7.02×10^7	4.31×10^8	0.16
2	0.48	348	4.49	320	3.24	1.48×10^8	1.61×10^8	0.92
3	0.03	329	4.70	307	2.00	1.50×10^7	4.86×10^8	0.03
4	0.58	397	4.44	344	3.63	1.60×10^8	1.16×10^8	1.38
5	0.84	414	4.82	381	1.51	5.50×10^8	1.05×10^8	5.25
6	0.91	418	4.58	369	2.63	3.43×10^8	3.39×10^7	10.11
15	0.75	437	4.93	398	1.17	6.38×10^8	2.13×10^8	3.00
16	0.76	436	4.66	381	2.19	3.47×10^8	1.10×10^8	3.17

[a] All spectra were measured at 295 K. [b] Quantum yield is calculated relative to quinine (Φ_f = 0.55 in 0.1 M H$_2$SO$_4$).



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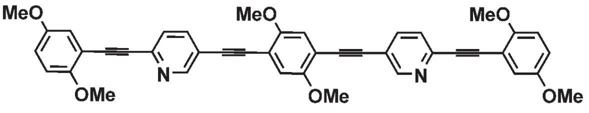

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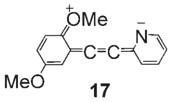
nylethynyl)benzenes (Φ_f: 0.50, λ_{em}: 345 nm for the *para* isomer; Φ_f: 0.14, λ_{em}: 330 nm for the *meta* isomer), and terphenyls (Φ_f: 0.54, λ_{em}: 342 nm for the *para* isomer; Φ_f: 0.039, λ_{em}: 331 nm for the *meta* isomer).[9] We previously reported the importance of π extension and donor/acceptor groups on the emission efficiency of the rod-shaped oligo(*p*-phenyleneethynylene)s.[10] The banana-shaped molecules **5** and **6**, which consist of alternately arranged pyridine (acceptor) and dimethoxybenzene (donor) rings, have a *meta*-substituted structure in addition to a *para*-substituted (rod-shaped) structure. Since oligo(*p*-phenyleneethynylene) has an almost acetylenic structure, even in the excited singlet state,[10,11] and the excited singlet state has a dipolar structure, the higher emission efficiency (Φ_f) of **5** and **6** relative to that of **15** and **16** might be explained by assuming that the emission efficiency depends on the movability of the dipolar structure (**17**) among the structurally equivalent donor/acceptor diads (dimethoxyphenylethynylpyridine units) in the excited singlet state molecules (in other words, the number of structurally equivalent dipolar diad units to **17**). The pyridine ring in the banana-shaped molecules (**5** and **6**) is able to move the dipolar structure **17** by both the half π bonds (C_2–N and C_6–N), while the pyridine ring in the rod-shaped molecules (**15** and **16**) is not able to move the dipolar structure because of the interruption of the dipolar structure.



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The fluorescence spectra of **5** and **6** are relatively sharp relative to that of **4** (Figure 1).

The effect of solvent on the emission efficiency of **5** and **6** is noteworthy (Table 2). Almost no solvent effect is observed for the absorption spectra of both **5** and **6**, while the fluorescence maxima of **5** and **6** are slightly shifted to longer wavelengths as the solvent polarity increases. Although the quantum yield of **5** is not similarly altered with a change in the solvent polarity, that of **6** remarkably decreases with an increase in the solvent polarity. The observed effect of the solvent on the Φ_f values of **5** and **6** can be interpreted by a change in the k_r and k_d values of **5** and **6** with a change in the solvent polarity: The k_r and k_d values for **5** are not so affected by solvent polarity. However, the k_r value of **6** decreases with an increase in solvent polarity even though the k_d value does not change, except for the cases of benzene and $CHCl_3$, where the k_d values decrease. The vastly different solvent dependency of the Φ_f values of **5** and **6** might be explained by the marked disparity between the distribution of the difference density (difference in the atomic charge in the excited state from that in the ground state) of **5** and **6**. The INDO/S difference density distribution (DDD) in the excited state of **5** and **6** is shown in Figure 2. It is evident that the marked change in the DDD in the excited state is not observed for **5**, while it is seen between the terminal regions and the central part of **6**, thus suggesting that the solvent polarity dependence of the Φ_f value should be negligible for **5**, but large for **6**.

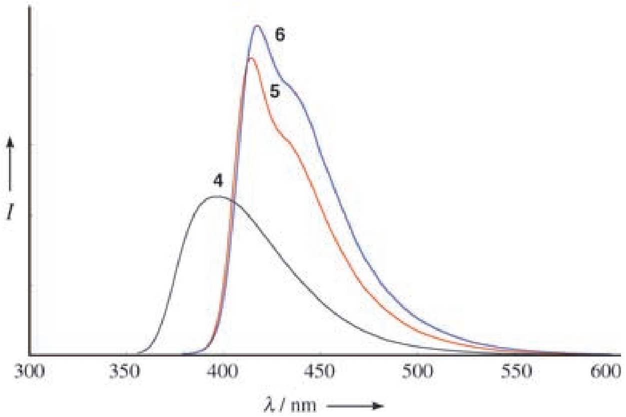


Figure 1. Fluorescence spectra of banana-shaped donor/acceptor oligo(aryleneethynylene)s **4** (black), **5** (red), and **6** (blue) in $CHCl_3$ at 295 K.

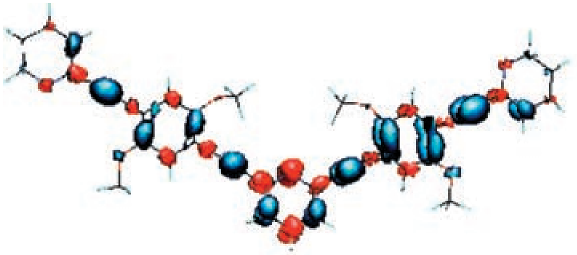
The behavior of banana-shaped molecule **3** having pyridine rings at both termini towards metal ions should be of interest in regard to the emission characteristics of the resulting complex.[12]

We have prepared the 1:1 complex **18** (Tf = trifluoromethanesulfonyl) both by reaction of a solution of **3** in CH_2Cl_2 with $[Ti^{IV}Cl_3]^+$ freshly generated from a solution of $TiCl_4$ in

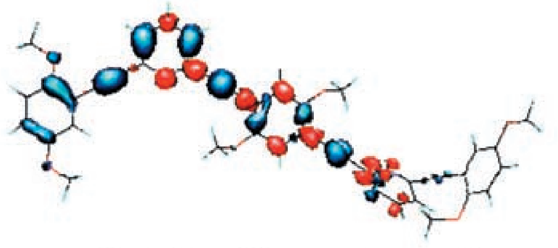
Table 2: Effect of solvent on the absorption and fluorescence characteristics of **5** and **6**.[a]

Compound	Solvent	Φ_f	λ_{em}[nm]	$\log\varepsilon$	λ_{abs}[nm]	k_r[s^{-1}]	k_d[s^{-1}]	k_r/k_d
5	C_6H_6	0.79	413	4.81	380	5.09×10^8	1.35×10^8	3.76
	$CHCl_3$	0.84	414	4.82	381	5.50×10^8	1.05×10^8	5.25
	THF	0.80	413	4.83	378	5.39×10^8	1.35×10^8	4.00
	CH_3CN	0.77	417	4.82	376	5.07×10^8	1.52×10^8	3.35
	DMF	0.82	422	4.80	379	5.18×10^8	1.14×10^8	4.56
	MeOH	0.76	425	4.84	379	5.25×10^8	1.66×10^8	3.17
6	C_6H_6	0.90	416	4.56	365	3.24×10^8	3.60×10^7	9.00
	$CHCl_3$	0.91	418	4.58	369	3.43×10^8	3.39×10^7	10.11
	THF	0.68	417	4.58	365	2.61×10^8	1.23×10^8	2.13
	CH_3CN	0.43	423	4.59	369	1.69×10^8	2.24×10^8	0.75
	DMF	0.48	427	4.56	367	1.75×10^8	1.89×10^8	0.92
	MeOH	0.42	427	4.61	371	1.71×10^8	2.36×10^8	0.72

[a] All spectra were measured at 295 K.

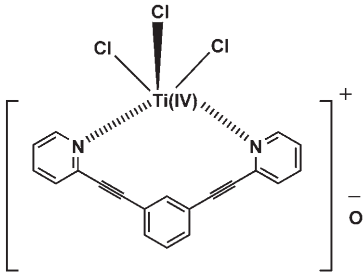


5 (excitation at 346 nm, calculated λ_{abs})



6 (excitation at 332 nm, calculated λ_{abs})

Figure 2. INDO/S difference density distribution of **5** and **6** in the excited singlet states (the red parts designate the atomic charges that are more negative in the excited state than in the ground state. The blue parts show the reverse situation. Colorless parts designate equal density in both the excited and ground states).



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CH_2Cl_2 and a solution of AgOTf in benzene, and by mixing **3** (in CH_2Cl_2) first with AgOTf (in benzene) and then adding $TiCl_4$ (in CH_2Cl_2).[13] Complex **18** is stable in the solid state, and does not dissociate in solution. However, its ligand **3** can be replaced by stronger ligand(s) such as 2,2′-bipyridine.

Although X-ray diffraction analysis of **18** has not yet been accomplished, because of difficulty in growing suitable single crystals, the MM2 structure (Figure 3) of **18** is very similar to that of the 1:1 Sb^V complex (**21**) of tetrakisareneazaarenecyclyne (**20**) with respect to the ligand **3** (see the Supporting Information).[14,15] The ^{1}H NMR spectroscopic and FAB MS data (Supporting Information) support this structure.[16]

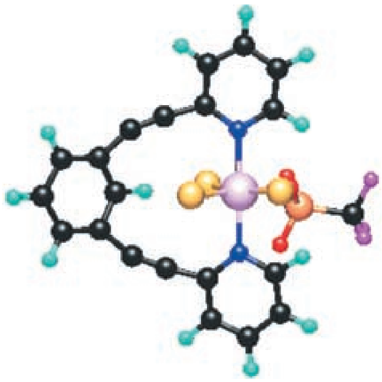


Figure 3. MM2 structure of **18**.

The absorption and fluorescence spectra of **18** are shown in Figure 4. The emission and absorption characteristics of **3** and **18–21** (**19:** trifluoromethanesulfonic acid salt of **3**) are summarized in Table 3.

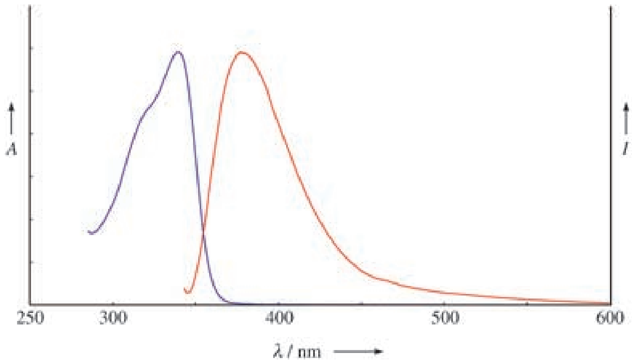
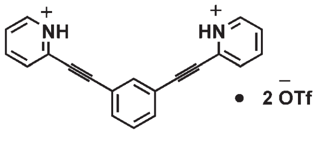


Figure 4. Absorption (blue) and fluorescence (red) spectra of **18** in CH_2Cl_2 at 295 K.

It is noted that the emission efficiency of **18** is about 60 times greater than that of **3**. An increase in the Φ_f value on formation of the metal bridge is also observed in **21**. In both cases, the k_d values decrease and the k_r values increase, thus resulting in an enhancement of the Φ_f value. Since a large increase in the Φ_f value is also seen for **19** (diprotonated **3**), the increase resulting from metal bridging is ascribed to the increase in the electron-accepting ability of the pyridine C=N groups by coordination to Ti^{IV} centers (formation of a positively charged sp^2 nitrogen atom).

In conclusion, we have created donor/acceptor banana-shaped molecules, and found that the donor/acceptor pentameric aryleneethyny-



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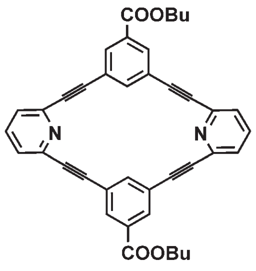

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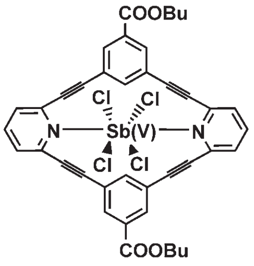

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Table 3: Emission and absorption characteristics of **3** and **18–21** in CH_2Cl_2.[a]

Compound	Φ_f[b]	λ_{em}[nm]	$\log\varepsilon$	λ_{abs}[nm]	τ[ns]	k_r[s^{-1}]	k_d[s^{-1}]	k_r/k_d
3	0.01	328	4.70	306	1.98	5.06×10^6	5.01×10^8	0.01
18	0.63	378	4.79	339	1.62	3.90×10^8	2.29×10^8	1.70
19	0.60	378	4.76	340	1.75	3.45×10^8	2.28×10^8	1.52
20	0.18	355	4.62	322	2.40	7.50×10^7	3.42×10^8	0.22
21	0.41	433	4.62	355	3.47	1.18×10^8	1.70×10^8	0.70

[a] All spectra were measured at 295 K. [b] Quantum yield is calculated relative to quinine (Φ_f=0.55 in 0.1 M H_2SO_4).

lenes (**5** and **6**) with single and double banana structures are highly efficient light emitters despite the interruption of the π conjugation. The emission efficiency is interpreted in terms of k_r and k_d values. A new concept on movability of the dipolar dimethoxyphenylethynylpyridine structure (in other words, the number of dipolar diad units structurally equivalent to **17**) in the excited singlet state molecules is presented to explain the results. A quite contrasting effect of the solvent on the emission efficiency was observed for **5** and **6**, which might be explained by the marked disparity between the difference density distribution in the excited states of **5** and **6**. The emission efficiency of **3** (very weak fluorophore) was found to dramatically increase on formation of a Ti^{IV} complex. The main reason for this is ascribed to the increase in the electron-accepting ability of the pyridine C=N groups by the coordination to Ti^{IV} centers.

Received: June 24, 2005

Keywords: C–C coupling · conjugation · luminescence · solvent effects · titanium

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