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7,7,8,8-Tetracyanoquinodimethane (TCNQ) emits visible photoluminescence in solution

Honami Tamaya, Hideyuki Nakano, Toshifumi Iimori*

Department of Applied Chemistry, Muroran Institute of Technology, Muroran 050-8585, Japan

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ABSTRACT

7,7,8,8-Tetracyanoquinodimethane (TCNQ) has been used as a versatile building block for designing organic conductors and assemblies. It is believed that the fluorescence quantum yield of TCNQ is extremely low and it does not show observable fluorescence. Here we report, contrary to the conventional beliefs, that TCNQ emits blue photoluminescence in nonpolar solution. The photoluminescence intensity acutely decreases with increasing solvent polarity. Our findings will facilitate the design of TCNQ-based materials for applications in optoelectronics and polarity sensors.

1. Introduction

The electron acceptor molecule TCNQ is an important molecule in chemistry and materials physics and is known as a versatile building block that can produce a number of functional solids and molecular assemblies. TCNQ forms charge-transfer complexes having high electrical conductivity with a variety of electron donor molecules or metals [1–5]. A prominent example is the salt of TCNQ with electron-donating tetrathiafulvalene (TTF) discovered in 1973, which was the first organic conductor to exhibit metallic conductivity [6–8]. Since then, TTF-TCNQ has been the prototype system in a fertile field of organic conductors and magnets. In addition, TCNQ and its derivatives have been utilized as components in assembling Langmuir-Blodgett films [9], organic field-effect transistors [10,11], and nonlinear optical materials [12].

The electronic state and the structure of TCNQ have extensively been investigated by photoelectron spectroscopy, vibrational spectroscopy, and theoretical calculations since 1960s [13–18]. A few studies on the photoluminescence of TCNQ have been reported to date, and the fluorescence and phosphorescence quantum yields (QY) of both TCNQ and the anion radical $TCNQ^{\bullet -}$ are known to be close to zero [19–21]. The efficient deactivation process in the first excited singlet (S_1) state has been ascribed to internal conversion (IC) [19], but excited state dynamics of TCNQ are still not well understood. The photoluminescence of some derivatives of TCNQ was reported by Bloor et al. [22], but the fluorescence QY was below 0.015 in monohydric alcohols. If TCNQ exhibited photoluminescence, then it would also be a useful building block to produce multifunctional materials that are both conducting and luminescent.

Here, we report that TCNQ unexpectedly exhibits fluorescence with a QY of ca. 0.1 in nonpolar solvents. In addition, the photoluminescence of TCNQ shows an acute response to subtle changes in the polarity of the solvent, and the fluorescence QY decreases with increasing solvent polarity. Our findings deepen the understanding on the property of TCNQ, and may facilitate the investigation and design of TCNQ-based materials for organic optoelectronics.

2. Experimental methods

TCNQ (Tokyo Chemical Industry) was recrystallised with acetonitrile and washed with benzene. Hexane (Wako Pure Chemical Industries, spectrochemical analysis grade), cyclohexane (Wako Pure Chemical Industries, spectrochemical analysis grade), dichloromethane (Junsei Chemical, fluorescence spectroscopy grade), carbon tetrachloride (Wako Pure Chemical Industries, super special grade), chloroform (Junsei Chemical, absorption spectroscopy grade), and acetonitrile (Junsei Chemical, fluorescence spectroscopy grade) were used as received without further purification. The concentration of TCNQ in the solutions was adjusted to $\sim 2 \times 10^{-6}$ mol/L in order to make the absorbance at the absorption maximum ca. 0.1. Prior to use in fluorescence measurements, the solutions were bubbled with Ar gas, handled in an Ar gas-filled glove box, and contained in a stoppered quartz cell with an optical path length of 1 cm, unless otherwise noted. The emission spectra were measured at a right angle to the excitation light. The fluorescence decay and the fluorescence quantum yield (QY) were measured by using the Quantaurus-Tau and Quantaurus-QY instruments (Hamamatsu Photonics), respectively. The variation of the excitation light intensity at different excitation wavelengths was evaluated by using a quantum counter of rhodamine B in ethylene glycol

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* Corresponding author.
E-mail address: iimori@mmm.muroran-it.ac.jp (T. Iimori).

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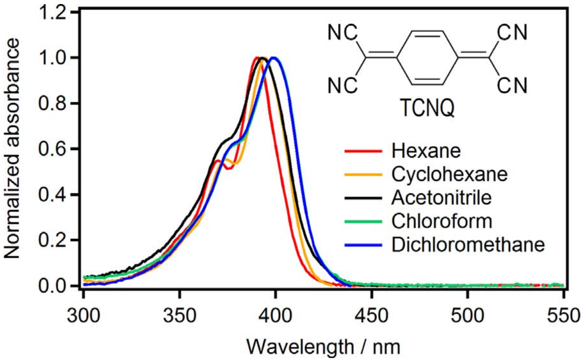

Fig. 1. Absorption spectra of TCNQ in different solvents.

[23]. The fluorescence intensity presented in this work was corrected for the variation of the excitation light intensity.

3. Results and discussion

Absorption spectra of TCNQ in a variety of solvents are shown in Fig. 1. The spectrum in nonpolar hexane clearly exhibits two vibronic bands at 391 and 370 nm, with relatively narrow band widths. A similar band shape was observed for cyclohexane, although the absorption maximum was red-shifted relative to that for hexane. The vibronic bands broadened for the other solvents with higher polarity, and the vibronic band at ~376 nm appeared as a shoulder band. A solvatochromic shift of the absorption maximum was also observable. For example, the absorption maxima in hexane, cyclohexane, and dichloromethane were 391 nm, 394 nm, and 401 nm, respectively. Linearity of the plots of solvatochromic shift versus solvent polarity was not observed, however (Fig. 2).

Fluorescence spectra are shown in Fig. 3. The excitation wavelength for each of the solvents was the corresponding absorption maximum (Table 1). The fluorescence intensity showed a drastic dependence on the solvent polarity: TCNQ exhibited relatively strong fluorescence intensity in the nonpolar solvents hexane and cyclohexane, whereas the fluorescence intensity in the three polar solvents was approximately 2×10^{-3} times weaker than that in hexane. In general, both hexane and cyclohexane are classified as typical nonpolar hydrocarbons with similar characteristics. However, the fluorescence intensity in cyclohexane was 0.7 times that in hexane. The dielectric constant actually differs between the two solvents, and in fact the Onsager polarity functions $f(D)$ are 0.37 and 0.41 for hexane and cyclohexane, respectively [24]. In this experiment, the absorbance at the absorption maximum for each solution was adjusted to ca. 0.1, which was small enough that the so-called inner filter effect was negligible [23]. Moreover, the fluorescence intensity was normalized to the absorbance at the wavelength of the excitation to correct a small inevitable variation in the concentration of TCNQ for each of the prepared solutions. Subsequently, the relative fluorescence QY for each of the solutions can be approximately represented by the observed fluorescence intensity. The observed results indicate that the fluorescence QY of TCNQ in solution is highly sensitive to the solvent properties. The band shape also changes with the solvent. In hexane and cyclohexane, the fluorescence band has a vibronic structure, whereas in the polar solvents, the vibronic structure nearly disappears. The sharp bands appearing in the range of 435 nm to 460 nm are assigned to the Raman scattering of the solvents.

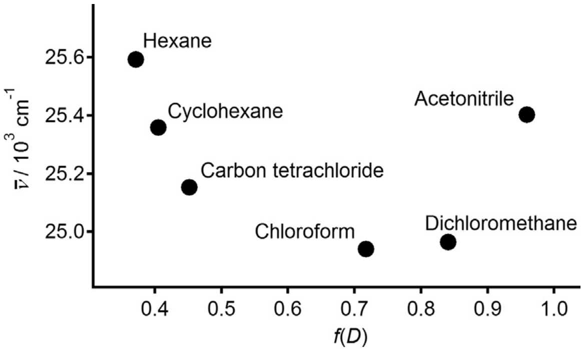

Fig. 2. Solvatochromic plot of the absorption maximum ($\bar{\nu}$) versus the polarity function ($f(D)$) of solvents.

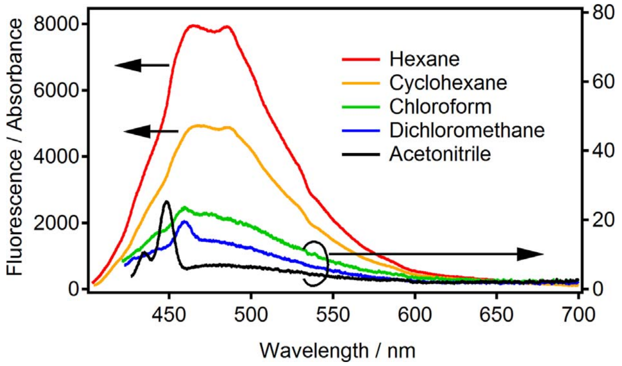

Fig. 3. Fluorescence spectra in different solvents. The fluorescence intensity was divided by the absorbance at the absorption maximum for each of the solutions. The intensity of the spectra for hexane and cyclohexane is shown on the left axis, and the intensity of the spectra for the other solvents is shown on the right axis.

Table 1
Absorption maximum (λ_{abs}) of TCNQ in different solvents.

Solvents	$f(D)$[a]	λ_{abs} / nm
Hexane	0.37	391
Cyclohexane	0.41	394
Carbon tetrachloride	0.45	397
Chloroform	0.72	401
Dichloromethane	0.84	401
Acetonitrile	0.96	393

[a] The Onsager polarity function of the solvents [24]. $f(D) = 2(D - 1)/(2D + 1)$, where D is the dielectric constant of the solvent.

Photographs of the solutions of TCNQ in hexane and dichloromethane are shown in Fig. 4. As inferred from the fluorescence maximum at 465 nm in Fig. 3, TCNQ in hexane exhibits pale blue fluorescence. Fluorescence was not observed in dichloromethane. The high sensitivity of the fluorescence QY to the solvent properties can be demonstrated in a solvent-mixing experiment. The fluorescence of TCNQ in hexane vanishes upon the addition of only one drop of pure

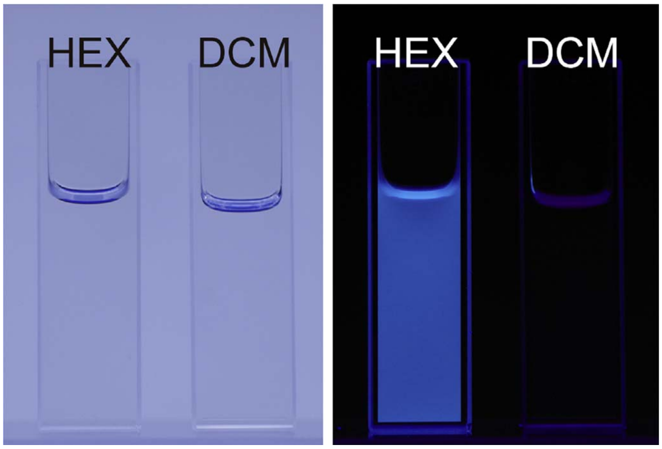

Fig. 4. Photographs of TCNQ in hexane (HEX) and dichloromethane (DCM). (Left) Under room light. (Right) Under photoexcitation at 365 nm.