Syntheses and Physical Properties of Carbazole-Phthalonitrile-Hybridized Light-Emitting Materials

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Abstract A series of carbazole-phthalonitrile hybridized light-emitting materials having expanded π-systems at the carbazole moieties were synthesized, and their physical properties such as cyclic voltammogram, UV-vis absorption spectra and photoluminescence spectra in solution and the solid states. These measurements showed that 5-carbazolyl-1, 3-phthalonitriles have more largely expanded π-systems than 2-carbazolyl-1, 3-phthalonitriles to exhibit bathochromic shifts in UV-vis absorption and emission spectra. Amino-substituted derivatives served as acid-sensors in CH₂Cl₂, and the intensities of their photoluminescence increased in accordance to the amount of 10-camphorsulfonic acid added.

Keywords: carbazole, phthalonitrile, TADF, emission, sensor, amino group.

Organic electro-luminescence (OEL) attracts a great attention because EL enables light, thin and flexible displays.1) Because organic molecules can be synthesized as we design, various light-emitting organic materials have been developed. Recently, Adachi group revealed that TADF (Thermally Activated Delayed Fluorescence) materials served well as light-emitting material which could overcome their theoretical maximum of external quantum efficiency (EQE) in OLEDs (organic light-emitting device).2) In TADF, electro-luminescence is enhanced by thermally promoted up-conversion of triplet state to singlet state because the TADF emitter is designed to realize a small energy difference (∆E_ST) between the first singlet (S₁) and triplet (T₁) excited states. Adachi group reported that dimeric carbazole-phthalonitrile-hybrid molecules 26IPNDCz and 35IPNDCz served as TADF light-emitting material to achieve EQE = 9.6% and 9.2%, respectively (Fig. 1).3) Although in this paper, it was noted that 35IPNDCz-based OLED exhibited larger EQE roll-off at high current density than 26IPNDCz counterpart (at 0.05 => 100 mACm⁻², 9.2 => 1.4% and 9.6 => 4.3%, respectively, effects of their structure deviation (2,6- vs 3,5-phthalonitriles) to their physical properties were not investigated. We were intrigued in electronic interaction between carbazole and phthalonitrile moieties in 26 and 35IPNDCz and synthesized a series of carbazole-phthalonitrile-hybrid molecules having expanded π-systems at carbazole moieties in order to investigate their physical properties. We herein report the syntheses of 2-carbazolyl-1,3-phthalonitriles 1 and 5-carbazolyl-1,3-phthalonitriles 2 and their physical properties such as cyclic voltammogram, UV-vis absorption, photoluminescence in solution and in the solid state and proton-sensing of amino derivatives.

Firstly, we synthesized two series of carbazolyl-phthalonitrile compounds (1 and 2) and 3,6,9-triphenylcarbazole (3) as shown Scheme 1. Syntheses of 2-carbazolyl-1,3-phthalonitriles 1 were achieved by two-step transformations from 4: nucleophilic substitution of 5 with 4 in the presence of K₂CO₃ in DMF provided 6 in 59% yield, and bromo substituents in 6 was converted to carbazole (3a), phenylethynyl (3b) and amino group. A series of 3-carbazolyl-1,5-
Phthalonitriles 2 were prepared similarly in two-step processes from 4: the transition-metal catalyzed couplings transformed 4 to 7a-c in moderate yields, and the subsequent nucleophilic substitution of 8 with 7a-c gave the desired derivatives 2a-c. Triphenylcarbazole 3 was obtained from CuI-1,10-phenanthroline-catalyzed coupling between 7a and phenyl iodide in 90% yield. Table 1 shows dihedral angles between carbazolyl and N-phenyl moieties of 1a-c, 2a-c, and 3 which were calculated at the B3LYP/6-31G(d) level. The density functional theory (DFT) calculations indicate that in their optimized structures, the dihedral angles of meta-dicyano derivatives 2a-c are smaller than the corresponding ortho-dicyano derivatives 1a-c leading to more effectively expanded π-systems in the meta derivatives as shown in Figs. 2a and 2b.

With a series of carbazole-phthalonitrile-hybrid compounds 1 and 2 in hand, their physical properties were investigated. Table 2 shows a summary of voltammograms of 1-3 in CH2Cl2 together with HOMO and LUMO potential levels of 1-3 calculated by DFT. The derivatives 1 and 2 exhibited reversible oxidation and reduction potentials, while 3 showed reversible two-step oxidation potentials but no reduction potentials. Meta-dicyano derivatives 2a,b undergo reduction and oxidation somewhat more facilely than the corresponding ortho-dicyano derivatives 1a,b: for instance, in oxidation of 1a and 2a, \( \text{HOMO}_{1/2} = 1.01 \) V (vs Fe/Fe3+) for 1a and 0.94 V for 2a. This result indicates...
that 2a,b has more largely expanded π-systems in comparison to 1a,b because of the efficient overlapping between π-systems of carbazole and phthalonitrile moieties in 2a,b. DFT calculations strongly support more efficient overlapping ascribable to the narrow dihedral angle of 2a as shown in Fig. 2b. In the redox potentials of 1c and 2c, both reduction and oxidation potentials of 2c were negatively shifted in comparison with 1c. The negative shifts could be explained in terms of electron-donating effect of Me₂N groups resulting in the higher potential energies of HOMO and LUMO in 2c. This result is consistent with the calculated HOMO and LUMO potential levels: 1c and 2c show the higher potential levels than 1a and 2a in the simulation (Table 2).

Fig. 3 shows UV-vis absorption spectra of 1, 2 and 3 in CH₂Cl₂ (1.0 x 10⁻⁴ mol/L), and these are summarized in Table 3. All the derivatives exhibit λ_max in a range of 253-341 nm. Phenyl (1a, 2a and 3) and aminophenyl derivatives (1c and 2c) showed large absorption bands (ε > 40 x 10³ L/(mol cm)) in a range of 250-300 nm and weak absorption bands having absorption edges around 390 nm. Phenylethynyl derivatives (1a and 2b) exhibited large absorption bands at 308 nm (ε 79 x 10³ L/(mol cm)), respectively. In the UV-vis absorption spectra, all the meta-dicyano derivatives showed slightly longer wavelengths of λ_max than the corresponding ortho-derivatives.

When UV light (275 nm) was irradiated to CH₂Cl₂ solutions and the powders of 1a and 2a, photoluminescence was observed (Fig. 4). Photoluminescence spectra of all the carbazole-phthalonitrile derivatives (1 and 2) and 3 were recorded in CH₂Cl₂ under N₂ (Fig. 5) and in the powdery state (Fig. 6), and a summary of these data was shown in Table 4 together with their photoluminescence quantum yields. In CH₂Cl₂, 3 exhibited strong emission having λ_PL_max at 390 nm, and it was found that a
fluorescence quantum yield of 3 (ΦF = 0.13) was larger than those of 1a,b and 2a,b (ΦF = 0.06 for each). Fluorescence quantum yields of 26IPNDCz and 35IPNDCz (ΦF = 0.72 and 0.50 in toluene, respectively)3) were remarkably larger than those of 1a,b and 2a,b. This could be ascribed to largely expanded π-system in bicarbazole units in 26IPNDCz and 35IPNDCz. Carbazole-phthalonitrile-hybrid derivatives 1a,b and 2a,b emitted photoluminescence at longer wavelengths than 3, but 1c and 2c showed no emission in CH2Cl2. Ortho-dicyano derivatives 1a,b and meta-dicyano derivatives 2a,b indicated the similar wavelengths at λPLmax, respectively, irrespective of the substituents on the carbazole: λPLmax = 473 nm for 1a, 472 nm for 1b and 514 nm for 2a, 511 nm for 2b. In emission of 2a,b, bathochromic shifts were observed in comparison to 1a,b, and these shifts demonstrate the efficient overlapping of π-systems between carbazole and phthalonitrile moieties in 2a,b. When UV light was irradiated to 1-3 in the powdery state, all the derivatives 1-3 exhibited emission, and it was observed that the wavelengths of λPLmax for 1a,b and 2a,b were shorter than those in CH2Cl2 solution, while 3 showed the similar wavelengths of λPLmax in CH2Cl2 and the powdery state (390 nm and 391 nm, respectively). Emission spectra of meta-dicyano derivatives 2a,b were observed at longer wavelengths than ortho-dicyano derivatives 1a,b as seen in CH2Cl2 solution. Although in CH2Cl2 solution, Me2N derivatives 1c and 2c showed no emission, 1c and 2c emitted the stronger fluorescence in the powdery state than the other derivatives 1a,b and 2a,b: ΦF = 0.19 (1c), 0.29 (2c) and 0.06-0.09 (1a,b and 2a,b).

Because the carbazole-phthalonitrile-hybrid derivatives are composed by connecting a donor (carbazole) and an acceptor (phthalonitrile), they would undergo intramolecular charge-transfer from the carbazole to the phthalonitrile moieties when the hybrid derivatives are photo-excited by irradiation of UV light. In order to investigate in their intramolecular charge-transfer, emission spectra in various solvents were recorded for two series such as Ph-derivatives 1a 2a (Fig. 7, Table 5) and Me2N-C6H4 derivatives 1c, 2c (Fig. 8, Table 6). When emission spectra of 1a,c and 2a,c were recorded in six solvents having different polarities (solvent dielectric constant ε = 2.4-39), the emission profiles showed bathochromic shifts in accordance to polarity of the solvents (λPLmax = 466 nm in toluene, 513 nm in DMF). In toluene, ortho-derivative 1a exhibited longer wavelength in emission than meta-counterpart 2a, and this result was similar to emission of 26IPNDCz (λPLmax = 488 nm) and 35IPNDCz (470 nm) in toluene. The bathochromic shifts observed in emission of 1a,c and 2a,c indicate that in the photo-excited states, the carbazole-phthalonitrile-hybrid derivatives underwent charge transfer because the charge-separated state could be stabilized more efficiently in the polar solvents than the ground state, and the smaller energy

| Table 4 | Wavelengths of λPLmax and photoluminescence quantum yields of 1, 2 and 3. |
|---------|------------------|------------------|------------------|------------------|------------------|
|         | 1a | 1b | 1c | 2a | 2b | 2c | 3 |
| λPLmax in CH2Cl2 (nm) | 473 | 472 | 514 | 511 | 506 | 507 | 390 |
| ΦF | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.13 |
| λPLmax in powdery state (nm, ΦF) | 434 | 435 | 522 | 472 | 506 | 507 | 391 |
| ΦF | 0.07 | 0.06 | 0.19 | 0.09 | 0.07 | 0.06 | 0.21 |

*1.0 x 10⁴ mol/L under N₂. ¹ Absolute quantum yield under N₂. ² Not detected.

| Table 5 | Solvent effect on photoluminescence spectra of 1a and 2a. |
|---------|------------------|------------------|------------------|------------------|------------------|
|         | Toluene | CH2Cl2 | THF | CH3CN | MeCN | DMF |
| λPLmax of 1a [nm] | 466 | 472 | 471 | 473 | 515 | 513 |
| λPLmax of 2a [nm] | 465 | 506 | 506 | 504 | 525 | 526 |

*1.0 x 10⁴ mol/L.
would be released as fluorescence.

In the emission profiles of 1a,c were observed two local maxima, respectively: for instance, 1a showed 466 nm and 499 nm (shoulder) in toluene. In the polar solvents, these two local maxima of 1a underwent red-shifts, and in the polar solvents such as MeCN ($\epsilon = 39$) and DMF ($\epsilon = 38$), it was observed that the emission located at the longer wavelength was relatively stronger in comparison to the emission at the shorter wavelength.

Although 1a showed 47 nm of difference at $\lambda_{PL \text{ max}}$ of toluene and DMF, 2a did 63 nm. The larger difference of 2a demonstrates that intramolecular charge transfer proceeds more efficiently in meta-dicyano derivative 2a than 1a.

When emission profiles of 1c and 2c were recorded, large bathochromic shifts were observed, but in the more polar solvents than THF ($\epsilon = 7.5$), no emission was observed (Fig. 8, Table 6). Although the mechanism of the quenching is ambiguous so far, electron-donating effect of the Me$_2$N groups would play a pivotal role in the quenching$^9$.

In the emission spectra, 1c and 2c showed larger solvent effects than 1a,b and 2a,b: $\Delta\lambda_{PL \text{ max}}$ (toluene-CHCl$_3$) = 47 nm for 1c, 6 nm for 1a, 53 nm for 2c, 43 nm for 2a. The large solvent effects could be explained by their HOMOs and LUMOs located in a distance (Figs 9a and 9b) which would provide the large charge-separated states under the irradiation of UV light: DFT calculations exhibited that in 1c and 2c, HOMOs would be located mainly on the Me$_2$N-phenyl groups, and LUMO would be on the phthalonitriles.

Although Me$_2$N-C$_6$H$_4$ derivatives 1c and 2c, emitted no photoluminescence in CH$_2$Cl$_2$ as shown in Table 6, we expected that addition of organic acid would enable emission of 1c and 2c because coordination of protons to amino groups could cancel the electron-donating effect of Me$_2$N groups. When DFT calculations were performed on doubly protonated derivative ($1c+2H^+$), it was suggested that coordination of protons to amino groups would enhance the HOMO-LUMO transition because of their efficient overlapping to result in the larger oscillator strength ($f = 0.0533$) (Fig. 10). When photoluminescence spectra of 1c and 2c were recorded in the presence of 10-camphorsulfonic acid (CSA, $\theta$ - 2.5 equivalents), remarkable enhancements in emission of 1c and 2c were observed (Fig. 11). The emission of 1c

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**Table 6** Solvent effect on photoluminescence spectra of 1c and 2c$^a$.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{PL \text{ max}}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>472</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>519</td>
</tr>
<tr>
<td>THF</td>
<td>$\text{nd}^b$</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>$\text{nd}^b$</td>
</tr>
<tr>
<td>MeCN</td>
<td>53 nm for 1c, 53 nm for 2c, 43 nm for 2a</td>
</tr>
</tbody>
</table>

$^a$ 10 x 10$^{-5}$ mol/L. $^b$ not detected.

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![Excitation energy HOMO (140) $\Rightarrow$ LUMO (141) 515.5 nm ($f = 0.0016$)](image)

Excitation energy HOMO (140) $\Rightarrow$ LUMO (141) 515.5 nm ($f = 0.0016$)

![Excitation energy HOMO (140) $\Rightarrow$ LUMO (141) 364.8 nm ($f = 0.0533$)](image)

Excitation energy HOMO (140) $\Rightarrow$ LUMO (141) 364.8 nm ($f = 0.0533$)
and 2c was enhanced in accordance to the amount of CSA added, and fluorescence quantum yields (Φ_F) of 1c and 2c in the presence of 2.0 equivalents of CSA achieved to 0.05. The amino derivatives 1c and 2c served as sensing materials for acid, and 2c exhibited emission having λ_{PL max} at 472 nm in the presence of 0.3 equivalent of CSA, while 1c did no emission in the presence of 0.5 equivalent

In summary, we synthesized a series of carbazole-phthalonitrile-hybrid light-emitting materials. From the investigation of their physical properties such as cyclic voltammogram, UV-vis absorption and photoluminescence, meta-dicyano derivatives have more efficiently expanded π-systems between carbazole and phthalonitrile moieties. By the investigation of solvent effect on their photoluminescence, it was revealed that all the derivatives underwent intramolecular charge-transfer when they were photo-excited by the irradiation of UV light. Although Me₂N-C₆H₄ derivative exhibited no emission in CH₂Cl₂, the proton coordination to Me₂N groups by the addition of organic acid CSA enhanced the emission. Further syntheses of the carbazole-phthalonitrile-hybrid derivatives and their application to light-emitting materials are under investigation.

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References

7) DFT calculations were performed using Gaussian ’09 program package
8) Although the amino-substituted derivatives 1c and 2c showed smaller dihedral angles (68 and 49°, respectively), electron-donating effect of amino group might produce some effect
9) The large bathochromic shifts of 1c and 2c in solution could be explained in terms of twisted intramolecular charge-transfer (TICT), but for explanation of the quenching in the polar solvents, further consideration would be required. See chapter 3 in "Molecular Fluorescence: Principles and Applications", B. Valeur, Ed.; VCH: Weinheim(2001)
10) The higher sensitivity of 2c could be explained by a larger oscillator strength (f = 0.3629) of dication (2c⁺2H⁺)
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