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Molecular ordering of photoreactive nonmesogenic 1,3,5-triazine compounds into columnar mesophases by charge transfer interaction

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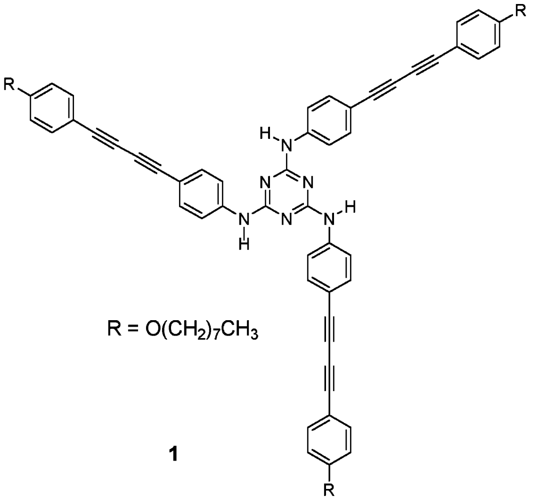
Abstract—1,3,5-Triazine compounds having diacetylenic groups and their charge transfer complexes with 2,4,7-trinitrofluoren-9-one (TNF) were prepared. The morphological changes were studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD) measurement. Although the 1,3,5-triazine compounds did not exhibit a mesophase, the charge transfer (CT) complexes with various mole ratios of TNF assembled into liquid crystalline phases. The CT complexes were UV-irradiated in the liquid crystalline (LC) state to yield oligomers.

Charge transfer (CT) interaction has attracted a great interest in the formation of liquid crystals.[1] Many potential mesogenic molecules having extended aromatic cores are electron-rich, and therefore, suitable for the CT complex formation with flat electron-deficient molecules, e.g. 2,4,7-trinitrofluoren-9-one (TNF).[1–3] Especially with aromatic discoid molecules, a face-to-face type intercalated stacking between electron donors and acceptors can occur, forming columnar phases. Ringsdorf et al. first observed CT induced nematic columnar (N_{Col}) phases in the mixtures of TNF with amorphous side-chain polymers carrying 2,3,6,7,10,11-hexasubstituted triphenylene moieties and columnar hexagonal (Col_{ho}) phases with related main-chain polymers.[4,5] Since then, CT interactions between various electron donors and acceptors have been employed to stabilize and modify mesophases.[4–15] In some cases, a CT interaction can induce a mosogenic phase even in a mixture of nomesogenic compounds.[4,5,7,9,13,14,16–19]

In the previous work, we reported a polymerizable 1,3,5-triazine derivative (**1**) (Scheme 1), where diphenyldiacetylenic groups were connected to a triazine ring via secondary amino linkages with alkyloxy tails in the periphery.[20] The compound exhibited a hexagonal columnar mesophase. When amino linkages were replaced by ether groups, however, the compound did not show mesomorphic ordered structures. We presumed that intermolecular hydrogen bondings of secondary amino groups and π–π interactions between aromatic rings played an important role in molecular ordering. In the further study, we prepared several derivatives having different numbers of phenyl rings to see the effect of π–π interactions between aromatic rings on the stacking of the molecules. No columnar mesophase formed in the absence of the second phenyl



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Scheme 1.

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ring at C4 of a butadiynyl side group probably because the face-to-face interaction was not strong enough for stacking. Recently, Janietz et al. reported the CT complexation of 2,4,6-triarylamino-1,3,5-triazines with electron acceptors, where the triazines acted as good electron donors.[12] The triazines exhibited hexagonal columnar phases, while the CT complexes formed lamellar structures. We expected similar interactions of the nonmesogenic 1,3,5-triazines with electron acceptors and investigated the induction of mesomorphic structures through CT interactions. Here we report the liquid crystalline properties of the CT complexes of the nonmesogenic 1,3,5-triazines with TNF and their photoreactions.

Scheme 2 illustrates the synthetic routes to the 1,3,5-triazine compounds.[21] CT complexes were prepared by dissolving the 1,3,5-triazine compounds and TNF in methylene chloride, stirring for 4 h, evaporating the solvent, and drying the residues in a vacuum. The triazine compounds and TNF were pale yellow powders. When they were dissolved in methylene chloride, the color of the solutions changed to deep red, indicative of CT complex formation.

The thermal transition data of the triazine compounds and their equimolar complexes with TNF are shown in Table 1. DSC and POM study revealed that the triazine compounds did not form mesomorphic structures. However, when complexed with TNF in the mole ratio of 1:1, they exhibited mesophases. In DSC thermograms of the complexes, the characteristic peaks of the single compounds disappeared, and new exotherm peaks corresponding to isotropic (I) to liquid crystalline (LC) transitions appeared at 121, 130, and 137°C on cooling for **5**:**TNF**, **6**:**TNF** and **7**:**TNF** complex, respectively. Figure 1 shows DSC thermograms of compound **6** and **6**:**TNF** complex. For **6**:**TNF** complex, a typical texture of a columnar mesophase appeared in the LC state,[22] and was maintained even at room temperature (Fig. 2). Other complexes also showed similar thermal behaviors.

Table 1. Phase transition temperatures and enthalpies (J g^{-1}) of the triazine compounds and their equimolar complexes with TNF

Complex	Phase transition temperature (°C)	
	2nd heating	2nd cooling
5:**TNF**[a]	LC 126(3.5) I	I 121(3.7) LC
6	K 64(0.8) I	I 60(0.6) K
6:**TNF**	LC 134(3.8) I	I 130(3.8) LC
7	K 77(1.3) I	I 74(1.5) K
7:**TNF**	LC 140(4.0) I	I 137(4.1) LC

[a] In case of compound **5**, either endotherm or exotherm was hardly detected on DSC traces.

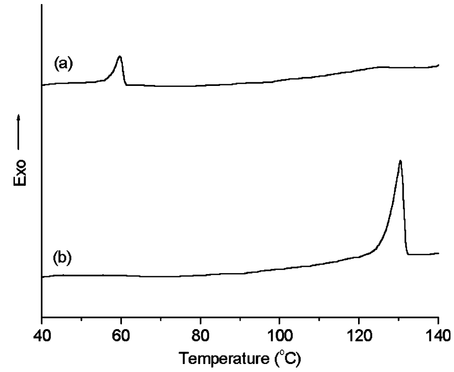
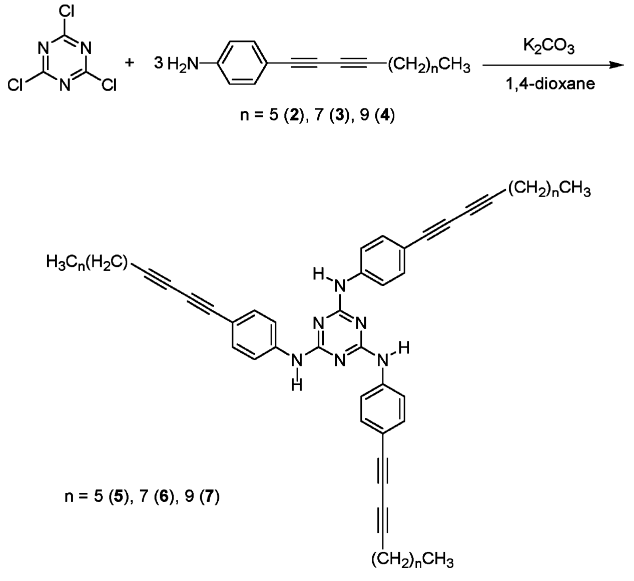


Figure 1. DSC thermograms of (a) compound **6** and (b) **6**:**TNF** complex on cooling at a rate of 10 K min^{-1}.



Scheme 2.

The structures of the complexes in the liquid crystalline (LC) phases were investigated by XRD. **5**:**TNF**, **6**:**TNF** and **7**:**TNF** complex in the LC state were quenched to room temperature and subjected to XRD experiments. In the X-ray diffractogram of **6**:**TNF** complex, a sharp, intense reflection in the small angle region, which corresponds to intercolumnar spacing of 35.3 Å and a diffuse scattering around 4.24 Å in the wide angle region, which corresponds to the reflection of alkyl chains, were observed. In addition, a broad shoulder

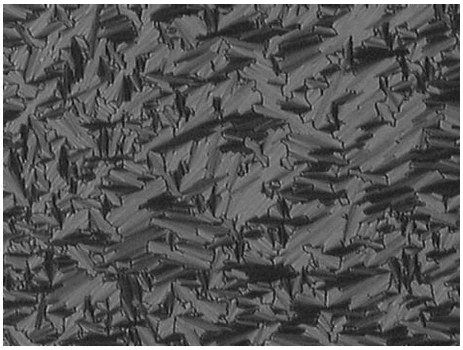


Figure 2. Polarizing optical micrograph of **6**:**TNF** complex on cooling at a rate of 10 K min^{-1}.

around 3.50 Å assigned to the average spacing of the disk–disk distance perpendicular to the plane of disk appeared, which indicates an irregular stacking of the disks (Fig. 3).[23] Since there appeared only one peak in the small angle region, it is difficult to further assign the arrangement of the columns. However, the texture of the LC phase strongly suggests the long range ordering of the columns. For **5**:**TNF** and **7**:**TNF** complex, the similar XRD results were obtained.

6:**TNF** complexes containing various mole ratios of TNF (40, 30, 20, and 10 mol%) were also prepared. DSC thermograms show that the isotropic transition temperatures of the complexes with different mole ratios were much dependent on the mol% of TNF (Table 2 and Fig. 4). As shown in Table 2, as the mol% of TNF increased, the temperature and enthalpy for the I→LC transition increased. Compared to the I→K transition enthalpy of compound **6**, the I→LC transition enthalpy of **6**:**TNF** complex containing 50 mol% of TNF was several times higher. This result indicates that strong interactions between **6**:**TNF** complexes through charge transfer occurred. The complexes with 40 mol% and with 30 mol% of TNF exhibited similar textures to that of the complex with 50 mol% of TNF. In the case of the complex with 20 mol% of TNF, a texture was developed partly. When 10 mol% of TNF was added, the complex did not have the distinct texture.

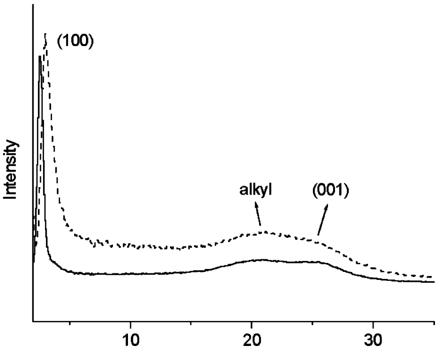


Figure 3. X-Ray diffractograms of **6**:**TNF** complex before UV-irradiation (solid line) and after UV-irradiation (dashed line) for 8 h in the LC state.

Table 2. Phase transition temperatures and enthalpies (J g^{-1}) of compound **6** and its complexes with TNF in various mole ratios

Complex	Mol% of TNF	Phase transition temperature (°C)	
		2nd heating	2nd cooling
6	0	K 64(0.8) I	I 60(0.6) K
6:**TNF**	10	LC 82(0.9) I	I 77(1.1) LC
6:**TNF**	20	LC 98(1.6) I	I 94(1.9) LC
6:**TNF**	30	LC 112(2.2) I	I 109(2.1) LC
6:**TNF**	40	LC 125(2.5) I	I 121(2.5) LC
6:**TNF**	50	LC 134(3.8) I	I 130(3.8) LC

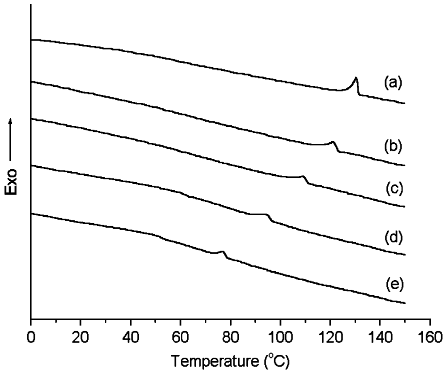


Figure 4. DSC thermograms of **6**:**TNF** complexes containing (a) 50 mol%, (b) 40 mol%, (c) 30 mol%, (d) 20 mol%, and (e) 10 mol% of TNF on cooling at a rate of 10 K min^{-1}.

Equimolar **6**:**TNF** complex was UV-irradiated in the LC state (125°C). In the FT-IR spectra, two weak bands at 2244 and 2152 cm^{-1} from symmetric and asymmetric stretching vibrations of carbon–carbon triple bonds appeared (Fig. 5). After UV-irradiation, the absorbances of two bands decreased, and a weak band at 2198 cm^{-1} for carbon–carbon triple bonds showed up. The broad and strong FT-IR shoulder around 1670 cm^{-1} for carbon–carbon double bonds was also observed. These results suggest that the photoreaction proceeded by 1,4-addition.[24–26] In the X-ray diffractogram of the equimolar **6**:**TNF** complex, the peak of the intercolumnar reflection became broad and its position changed slightly after UV-irradiation (Fig. 3). The UV-irradiated complex showed similar thermal behaviors to the unreacted one, except that it became very viscous in the LC state and the enthalpy value for the LC→I transition decreased gradually according to the reaction time. Based on IR and DSC results, consumption of diacetylenic groups by the UV-irradiation was estimated (Table 3). Since the UV-irradiated complex was soluble in organic solvents such as tetrahydrofuran, chloroform and methylene chloride, the photoreaction likely yielded only oligomers. This was attributed to the fact that the distance between diactylenic groups was increased by the intercalation of TNF, becoming unsuitable for the topochemical polymerization. The thermal polymerization of the complex

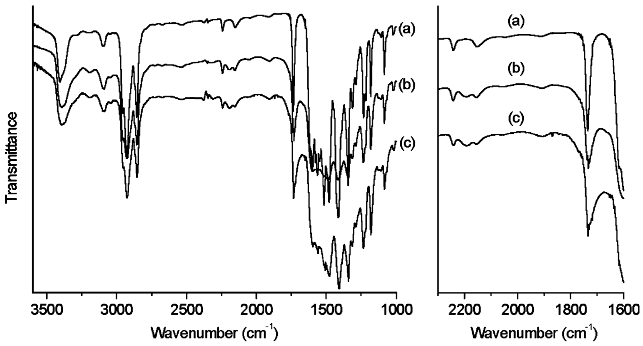


Figure 5. FT-IR spectra of equimolar **6**:**TNF** complex (a) before UV-irradiation, (b) after UV-irradiation for 4 h, and (c) 8 h.

Table 3. Phase transition temperatures and enthalpies (J g^{-1}) of equimolar **6**:**TNF** complex according to irradiation time

Irradiation time (h)	Conversion[a] (%)	Phase transition temperature (°C)	Enthalpy
0	–	134	3.8
4	22	131	2.3
8	54	131	1.3

[a] Conversion % was estimated by IR spectroscopy.

was also attempted. The complex was annealed for 16 h in the LC state (120°C), but no significant structural change was observed by IR spectroscopy.

In summary, 1,3,5-triazine compounds having diacetylenic groups and their complexes with various mole ratios of TNF were prepared. The triazine compounds did not exhibit mesophases, but their complexes displayed columnar mesophases. Equimolar **6**:**TNF** complex was UV-irradiated in the LC state to yield oligomers. However, thermal annealing of the complex in the LC state did not give rise to the reaction. FT-IR study on the UV-irradiated complex showed that the photoreaction proceeded by 1,4-addition.

Acknowledgements

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21. Compound **5**: To a solution of compound **2** (1.09 g, 4.84 mmol) in 1,4-dioxane (50 mL) were added cyanuric chloride (0.23 g, 1.24 mmol) and potassium carbonate (0.80 g, 5.80 mmol) under nitrogen. The reaction mixture was refluxed for 24 h. After removal of precipitates by filtration, the filtrates were concentrated to dryness by evaporation under reduced pressure. The product was isolated by column chromatography on silica gel (methylene chloride/hexane = 3/1); yield 0.65 g (70%). ^{1}H NMR (DMSO-d_6, 300 MHz): $\delta = 9.70$ (s, 3H, NH), 7.88, 7.48 (dd, 12H, aromatic ring protons), 2.41 (t, 6H, $-C{\equiv}CCH_2$,), 1.53–1.28 (m, 24H, $(CH_2)_4$), 0.88 (t, 9H, CH_3). IR (KBr, cm^{-1}): 3404, 3278, 3180, 3085, 2929, 2857, 2242, 2153, 1579, 1565, 1517, 1481, 1410, 1351. ^{13}C NMR (CDCl$_3$, 300 MHz) $\delta = 164.4$, 139.1, 133.6, 120.5, 117.2, 85.3, 75.1, 74.6, 65.6, 31.7, 29.0, 28.7, 22.9, 20.0, 14.5. Anal. calcd for $C_{51}H_{54}N_6$: C, 81.56; H, 7.25; N, 11.19. Found: C, 81.23; H, 7.32; N 11.18. Compound **6**: This compound was prepared by similar procedure to that described for compound **5** using compound **3** instead of compound **2**. The product was isolated by column chromatography on silica gel (methylene chloride/hexane = 2/1); yield 0.73 g (62%). ^{1}H NMR (DMSO-d_6, 300 MHz): $\delta = 9.66$ (s, 3H, NH), 7.87, 7.47 (dd, 12H, aromatic ring protons), 2.41 (t, 6H, $-C{\equiv}CCH_2$,), 1.51–1.27 (m, 36H, $(CH_2)_6$), 0.87 (t, 9H, CH_3). IR (KBr, cm^{-1}): 3409, 3292, 3185, 3096, 2923, 2853, 2244, 2152, 1569, 1558, 1521, 1481, 1416, 1352. ^{13}C NMR (CDCl$_3$, 300 MHz) $\delta = 164.4$, 139.1, 133.6, 120.5, 117.2, 85.3, 75.1, 74.6, 65.6, 32.2, 29.6, 29.5, 29.3, 28.7, 23.1, 20.0, 14.5. Anal. calcd for $C_{57}H_{66}N_6$: C, 81.97; H, 7.97; N, 10.06. Found: C, 81.92; H, 8.07; N, 10.04. Compound **7**: This compound was prepared by similar procedure to that described for compound **5** using compound **4** instead of compound **2**. The product was iso-

lated by column chromatography on silica gel (methylene chloride/hexane = 2/1); yield 1.00 g (75%). ^{1}H NMR (DMSO-d_6, 300 MHz): $\delta = 9.65$ (s, 3H, NH), 7.86, 7.46 (dd, 12H, aromatic ring protons), 2.40 (t, 6H, $-C{\equiv}CCH_2$), 1.50–1.26 (m, 48H, $(CH_2)_8$), 0.85 (t, 9H, CH_3). IR (KBr, cm^{-1}): 3405, 3281, 3180, 3090, 2924, 2853, 2243, 2153, 1581, 1566, 1518, 1480, 1410, 1350. ^{13}C NMR ($CDCl_3$, 300 MHz) $\delta = 164.2$, 138.9, 133.4, 120.3, 117.0, 85.0, 74.8, 74.4, 65.4, 32.1, 29.8, 29.7, 29.5, 29.3, 29.1, 28.5, 22.9, 19.8, 14.3. Anal. calcd for $C_{63}H_{78}N_6$: C, 82.31; H, 8.55; N, 9.14. Found: C, 82.27; H, 8.68; N, 9.15.

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