

# H-Bonded effects on supramolecular liquid crystalline trimers containing photoluminescent cores

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Received 14th February 2001, Accepted 10th August 2001

First published as an Advance Article on the web 9th October 2001

Several series of hydrogen-bonded (H-bonded) liquid crystalline trimers are constructed by complexation of two complementary components containing various bifunctional photoluminescent (PL) acceptor cores and monofunctional proton donors (in a 1 : 2 molar ratio). These supramolecular liquid crystalline trimers (*i.e.* H-bonded trimers **1/3**, **1/4**, **1/5**, **1/6**, **2/3**, **2/4**, **2/5** and **2/6**) are, respectively, obtained from bifunctional bis-pyridyl acceptors (containing conjugated benzene and thiophene centers) (**1** and **2**) complexed with monofunctional carboxylic acids (containing benzene, thiophene or naphthalene) (**3–6**) in a 1 : 2 acceptor–donor group stoichiometry. Though the PL bis-pyridyl acceptors (**1** and **2**) do not possess any mesophases, the distinct mesomorphism and supramolecular architecture of these H-bonded trimers are confirmed by polarizing optical microscopy (POM), DSC, and powder X-ray diffraction (XRD) experiments. Moreover, the PL properties of the photoluminescent bis-pyridyl cores can be adjusted not only by the central structures of the cores but also by their surrounding non-photoluminescent proton donors. In general, redder shifts occur in PL spectra of H-bonded trimers when proton donors of smaller  $pK_a$  values are H-bonded to the photoluminescent cores. Significantly, different wavelengths and polarized light of PL emission can be obtained in these supramolecular structures possessing both liquid crystalline and photoluminescent properties.

## Introduction

Recently, the application of hydrogen bonding in the formation of new liquid crystalline materials, *i.e.* supramolecular liquid crystals, has been rapidly developed.<sup>1–4</sup> Supramolecular liquid crystals are molecular complexes generated from complexation of molecular species through non-covalent interactions, *e.g.* hydrogen bonding. The mesogenic properties can be easily modified by miscellaneous proton donors and proton acceptors, and new liquid crystalline properties, which are different from those of their original moieties, can be obtained by the supramolecular structures. Many kinds of hydrogen bonds and building elements have been explored in the H-bonded structures to stabilize liquid crystalline phases.<sup>5–12</sup> Among these approaches, intermolecular hydrogen bonding is easily obtained by complexation of carboxylic (or benzoic) acid and pyridyl moieties. Owing to the ease of tailoring and modification of the supramolecular structures, the H-bonded liquid crystalline materials have various potential applications in the fields of display and electro-optical devices.

Regarding the linearity of the supramolecular liquid crystals, the most common rigid cores in the supramolecular liquid crystals are linear structures with *para*-substituted aromatic rings H-bonded through the pyridyl and carboxylic acid moieties. Nonetheless, some supramolecular liquid crystals with nonlinear structures were reported to reveal interesting mesomorphic properties.<sup>13–20</sup> Among these publications, our recent work shows that kinked supramolecules containing different bending sites provide the ability to manipulate the mesomorphic properties of the complexes using angular H-bonded interactions.<sup>17–18</sup> In addition, thiophene-based supramolecular liquid crystals make use of non-N-heterocyclic structures as the H-bonded moieties. The thiophene-based structures supplying dipoles and bent configurations in the

supramolecules can simultaneously reduce the phase transition temperatures of the supramolecules and improve the solubility of the moieties.<sup>16,19–20</sup> Novel mesomorphism has been successfully demonstrated by bending supramolecules and introducing dipoles in their centers through using a five-membered heterocyclic ring. This thiophene-based nonlinear structure with lone-pair electrons (not contained in the hydrogen bond) providing strong dipoles is applied to our H-bonded trimers as building blocks of either proton acceptors or donors. Consequently, different linkages and rigid parts containing various aromatic rings, including heterocyclic thiophene and fused naphthalene rings, are utilized to study their influence on these H-bonded trimers.

Recently, a series of photoluminescent bis-pyridyl compounds have been developed and made into doped-LED devices.<sup>21</sup> Since the bis-pyridyl compounds can be used as proton acceptors to form H-bonded trimers, several series of novel supramolecular liquid crystals containing these photoluminescent bis-pyridyl compounds are demonstrated in this report. Various mesogenic phases, including nematic, smectic A, and smectic C phases, were observed in these H-bonded trimers. The mesogenic properties can be tuned by the proton donors and the bis-pyridyl cores. Some previous research showed that the pH level of the conjugated copolymers containing pyridine units in polyelectrolytes has pronounced effects on the emission spectra.<sup>22–24</sup> Besides, some protonated products of bis-pyridyl derivatives have also been studied as laser dyes both in aqueous and in micellar media. To our knowledge, H-bonded effects on photoluminescent supramolecules in solid films have not been reported yet. So far, there are few reports on H-bonded photoluminescent materials giving liquid crystalline properties. Our preliminary results show that a red shift occurs in these H-bonded trimers when proton donors of smaller  $pK_a$  values are H-bonded to the

supramolecules. This is similar to the red shift in emission observed in previous polyelectrolytes in the aqueous form at lower pH values due to the protonation of the pyridine nitrogen. Therefore, we also would like to illustrate the H-bonded effects on the photoluminescence of these supramolecular liquid crystals in their solid state form.

## Experimental

### Characterization

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker MSL 200 or 300 spectrometer (200 or 300 MHz) from a  $\text{CDCl}_3$  or DMSO solution with TMS as the internal standard. The elemental analyses were carried out on a Perkin–Elmer 2400 CHN. The thermal transition temperatures and textures of all products were obtained from a Perkin–Elmer DSC-7 and Leitz Laborlux S polarizing optical microscope (POM) equipped with a THMS-600 heating stage. The heating and cooling rates were  $10\text{ }^\circ\text{C min}^{-1}$  for all measurements unless mentioned. Photoluminescence spectra were determined using a Hitachi F4500 fluorescence spectrophotometer and the concentrations of the solutions are less than  $5 \times 10^{-6}$  M. Powder X-ray diffraction (XRD) patterns were obtained from a Siemens D-5000 X-ray diffractometer (40 kV, 30 mA) fitted with a TTK450 temperature controller. Nickel-filtered  $\text{CuK}\alpha$  radiation was used as the incident X-ray beam.

### Synthesis

All compounds (1–6) used in this study were synthesized by previous methods<sup>20–21,25</sup> and they were identified as the required materials and judged to be pure by  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectroscopy.

**Compounds 1 and 2.** Both bifunctional bis-pyridyl compounds (1 and 2), *i.e.* 1,4-bis(4-pyridylethenyl)benzene **BPB** (1) and 2,5-bis(4-pyridylethenyl)thiophene **PTP** (2), were synthesized by following literature methods.<sup>21,25</sup>

**Compounds 3–6.** All monofunctional carboxylic acids (3–6), *i.e.* 4-decyloxybenzoic acid **C<sub>10</sub>OBA** (3), 6-decyloxy-2-naphthoic acid **C<sub>10</sub>ONA** (4), thiophene-2,5-dicarboxylic acid monodecyl ester **C<sub>10</sub>COOHA** (5) and terephthalic acid monodecyl ester **C<sub>10</sub>COOBA** (6), were synthesized by following previous methods.<sup>20</sup>

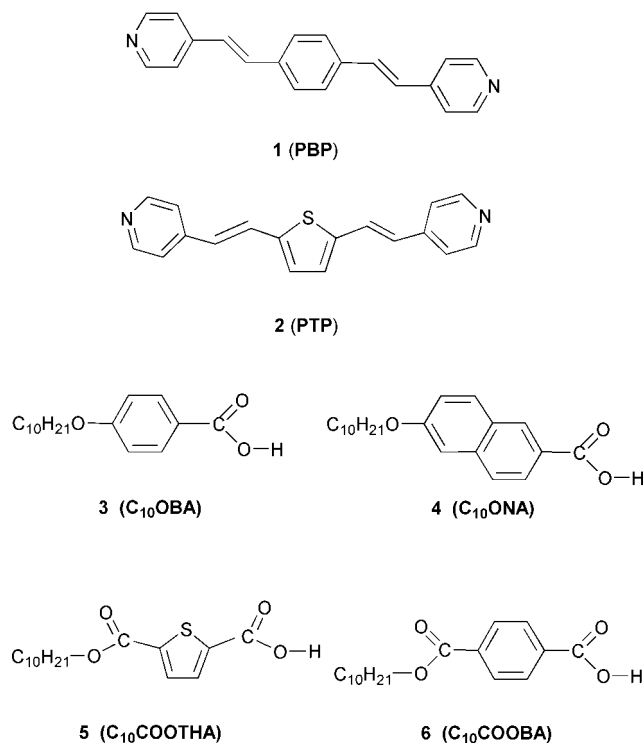
### Preparation of H-bonded trimers

H-bonded trimers, *i.e.* 1/3, 1/4, 1/5, 1/6, 2/3, 2/4, 2/5 and 2/6 (molar ratio 1 : 2), were prepared by slow evaporation of THF solution containing the mixtures of a 1 : 2 group molar ratio of the H-bonded acceptor and donor moieties, followed by drying *in vacuo* at  $60\text{ }^\circ\text{C}$ .

## Results and discussion

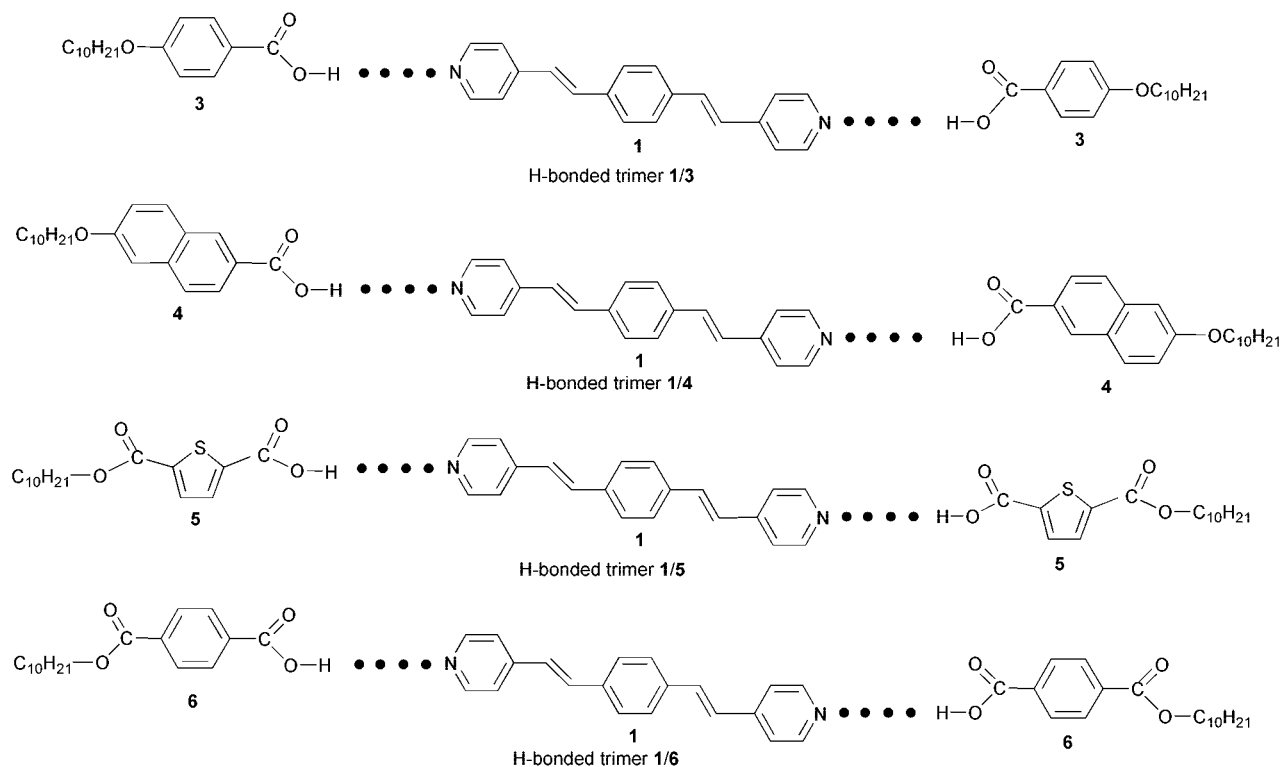
H-bonded trimers containing photoluminescent bis-pyridyl cores are obtained from bifunctional bis-pyridyl compounds (1 and 2) complexed with monofunctional carboxylic acids (3–6), *i.e.* 1/3, 1/4, 1/5, 1/6, 2/3, 2/4, 2/5 and 2/6 (molar ratio 1 : 2). All H-bonded moieties, *i.e.* acceptors (1 and 2) and donors (3–6), are listed in Fig. 1. The schematic structures of H-bonded trimers, *i.e.* H-bonded trimers 1/3, 1/4, 1/5 and 1/6 containing photoluminescent bis-pyridyl benzene core 1 and H-bonded trimers 2/3, 2/4, 2/5 and 2/6 containing photoluminescent bis-pyridyl thiophene core 2, are shown in Fig. 2 and Fig. 3, respectively.

The thermal properties of H-bonded trimers 1/3, 1/4, 1/5, 1/6, 2/3, 2/4, 2/5 and 2/6 (molar ratio 1 : 2) are shown in Table 1. The phase transition temperatures of these individual proton



**Fig. 1** Proton acceptors (1,2) and donors (3–6) used in H-bonded trimers.

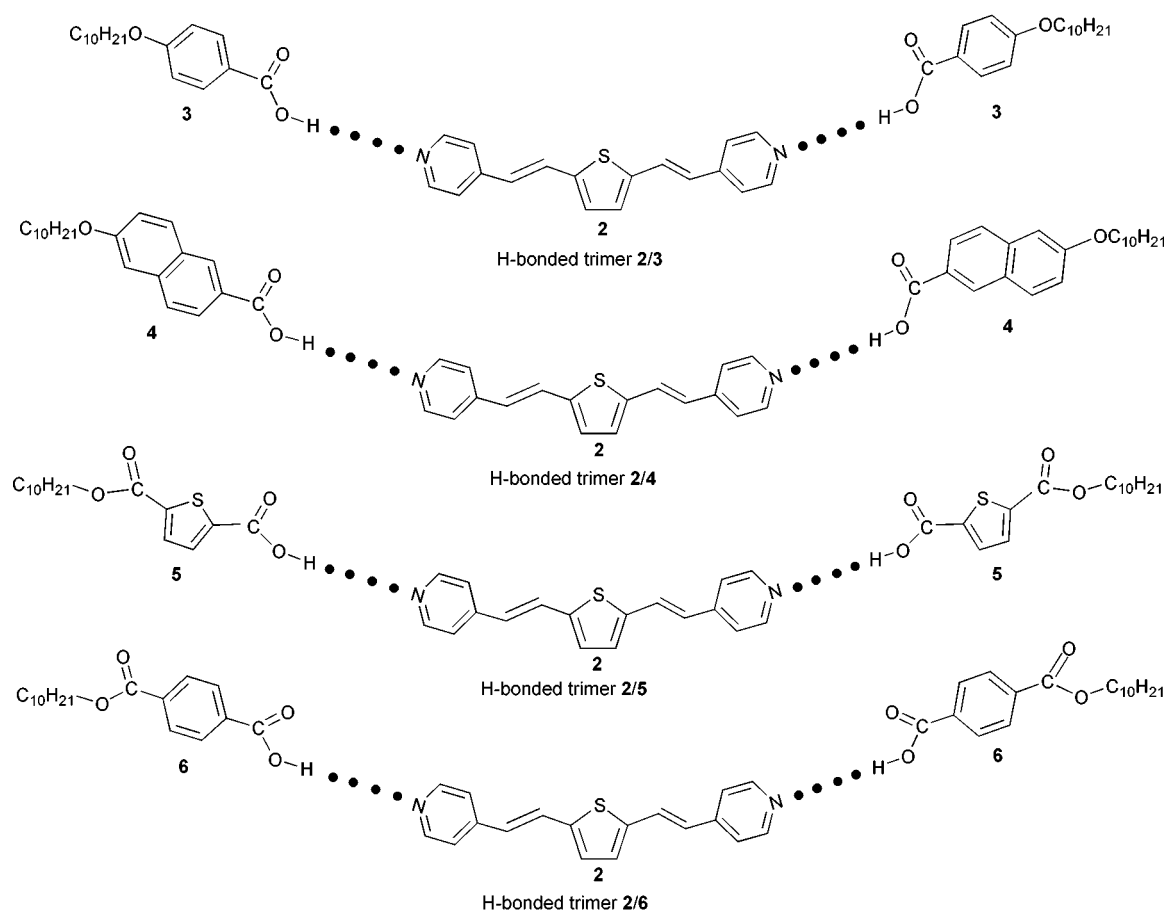
acceptors and donors, *i.e.* 1,4-bis(4-pyridylethenyl)benzene **BPB** (1), 2,5-bis(4-pyridylethenyl)thiophene **PTP** (2), 4-decyloxybenzoic acid **C<sub>10</sub>OBA** (3), 6-decyloxy-2-naphthoic acid **C<sub>10</sub>ONA** (4), thiophene-2,5-dicarboxylic acid monodecyl ester **C<sub>10</sub>COOHA** (5) and terephthalic acid monodecyl ester **C<sub>10</sub>COOBA** (6), are listed in the bottom appendix of Table 1. Most H-bonded acceptor and donor moieties show poor mesomorphism except that H-bonded donors 3 and 4 (forming H-bonded dimers) reveal  $S_C$  and  $N$  phases. Importantly, novel liquid crystalline properties (shown in Table 1), *i.e.*  $S_F$ ,  $S_C$ ,  $S_A$  and  $N$  phases, which are different from those of their original moieties, are obtained by the supramolecular structures and their phase diagram is illustrated in Fig. 4. It is observed that trimers 1/3, 1/4, 2/3 and 2/4 show the appearance of the  $S_A$  phase, and trimers 1/5, 1/6, 2/5 and 2/6 reveal the appearance of  $S_C$  and/or  $N$  phases. Compared with analogous H-bonded trimers containing the bis-pyridyl thiophene core (2), H-bonded trimers containing the bis-pyridyl benzene core (1) have higher clearing temperatures ( $T_C$ ), *e.g.* 1/3 > 2/3, 1/4 > 2/4, and so on. Furthermore, H-bonded trimers containing the bis-pyridyl benzene core (1) shown in Fig. 4 prefer to form or to broaden the  $S_C$  phase to a greater degree than those containing the bis-pyridyl thiophene core (2). However, H-bonded trimers containing the bis-pyridyl thiophene core (2) prefer to broaden the  $S_A$  phase and reduce the  $N$  phase to a greater degree than those H-bonded trimers containing the bis-pyridyl benzene core (1). Regardless of the central acceptor cores, similar phase behaviour occurs in the H-bonded trimers with the same proton donors, so their mesogenic properties might be mainly contributed from their proton donors. This can be explained by the higher molar ratio of donors in the H-bonded trimers (acceptor/donor molar ratio 1 : 2). For instance, the  $S_A$  phase is preferred in the H-bonded trimers consisting of donors with ether linkages (3 and 4), *i.e.* 1/3, 1/4, 2/3 and 2/4.  $S_C$  and  $N$  phases seem to be favored in the H-bonded trimers consisting of donors with ester linkages (5 and 6), *i.e.* 1/5, 1/6, 2/5 and 2/6. Another trend of the clearing temperatures happens in the series containing the proton donors 3, 4, 5 and 6, *e.g.* 2/4 (naphthalene donors) > 2/3 (benzene donors with ether linkage) > 2/6 (benzene donors with ester linkage) > 2/5 (thiophene donors), except for that in 1/6



**Fig. 2** The schematic structures of H-bonded trimers 1/3, 1/4, 1/5 and 1/6 (molar ratio 1 : 2) containing photoluminescent core 1.

(benzene donors with ester linkage) <1/5 (thiophene donors). In general, H-bonded trimers containing more rigid components (*i.e.* naphthalene donors compared with the other donors) and more linear shape (*i.e.* **PBP (1)** vs. the other

acceptor **PTP (2)**) may have higher clearing temperatures. Accordingly, the adjustment of the bis-pyridyl cores and proton donors in these H-bonded trimers can generate novel liquid crystalline properties.

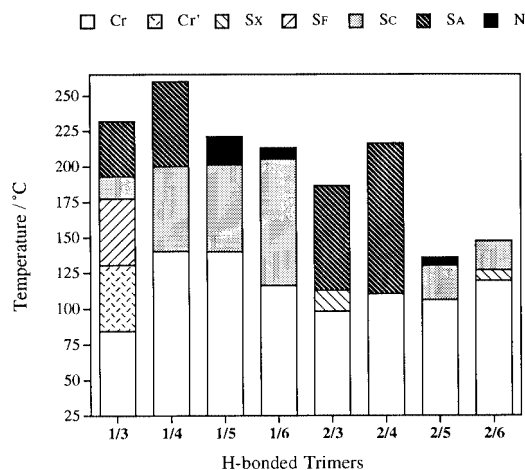


**Fig. 3** The schematic structures of H-bonded trimers 2/3, 2/4, 2/5 and 2/6 (molar ratio 1 : 2) containing photoluminescent core 2.

**Table 1** Phase transition temperatures ( $^{\circ}\text{C}$ )<sup>a</sup> and corresponding enthalpies ( $\text{J g}^{-1}$ ), in parentheses, of H-bonded trimers **1/3**, **1/4**, **1/5**, **1/6**, **2/3**, **2/4**, **2/5**, **2/6** (molar ratio 1:2) by complexation of 1,4-bis(4-pyridylethynyl)benzene **PBP** (**1**) or 2,5-bis(4-pyridylethynyl)thiophene **PTP** (**2**) with 4-decyloxybenzoic acid **C<sub>10</sub>OBA** (**3**), 6-decyloxy-2-naphthoic acid **C<sub>10</sub>ONA** (**4**), thiophene-2,5-dicarboxylic acid monodecyl ester **C<sub>10</sub>COOHA** (**5**) or terephthalic acid monodecyl ester **C<sub>10</sub>COOBA** (**6**)<sup>b</sup>

<b>1/3</b>	Cr	84.4 (3.6)	Cr'	130.4 (25.4)	S <sub>F</sub>	177.6 (7.9)	S <sub>C</sub>	193.0 (-) <sup>c</sup>	S <sub>A</sub>	231.8 (30.9)	I
		57.3 (2.8)		98.3 (22.8)		171.1 (7.6)		191.0 (-) <sup>c</sup>		226.5 (30.4)	
<b>1/4</b>	Cr	140.5 (64.6)					S <sub>C</sub>	200.0 (-) <sup>c</sup>	S <sub>A</sub>	260.1 (26.9)	I
		120.8 (47.4)						196.0 (-) <sup>c</sup>		253.6 (25.2)	
<b>1/5</b>	Cr	140.1 (57.6)					S <sub>C</sub>	201.1 (16.9)	N	221.0 (-) <sup>c</sup>	I
		104.5 (37.9)						193.0 (10.1)		215.0 (-) <sup>c</sup>	
<b>1/6</b>	Cr	116.0 (43.1)					S <sub>C</sub>	205.2 (15.4)	N	213.0 (3.5)	I
		83.4 (42.8)						195.4 (10.3)		210.0 (-) <sup>c</sup>	
<b>2/3</b>	Cr	98.0 (18.4)					S <sub>X</sub>	112.7 (41.9)	S <sub>A</sub>	186.5 (19.0)	I
		51.1 (12.7)						79.8 (36.0)		181.4 (15.4)	
<b>2/4</b>	Cr	110.3 (49.6)					S <sub>C</sub>	60.5 (-) <sup>c</sup>	S <sub>A</sub>	216.3 (15.3)	I
		54.7 (50.5)								209.7 (14.2)	
<b>2/5</b>	Cr	106.0 (43.1)					S <sub>C</sub>	130.0 (-) <sup>c</sup>	N	136.0 (8.4)	I
		57.8 (50.9)						128.0 (-) <sup>c</sup>		132.2 (5.8)	
<b>2/6</b>	Cr	119.5 (21.4)					S <sub>X</sub>	127.0 (41.2)	S <sub>C</sub>	147.5 (6.3)	I
		100.4 (19.4)						117.1 (38.7)		127.1 (8.0)	

<sup>a</sup>Phase transition temperatures and corresponding enthalpies were determined by the 2nd heating and cooling scans (at the heating and cooling rate of  $10^{\circ}\text{C min}^{-1}$ ); abbreviations: Cr, Cr'=crystalline phases, S<sub>X</sub>=unidentified smectic phase, S<sub>F</sub>=smectic F phase, S<sub>C</sub>=smectic C phase, S<sub>A</sub>=smectic A phase, N=nematic phase, I=isotropic liquid. <sup>b</sup>The phase transition temperatures (heating) of proton acceptor and donor moieties are as follows: 1,4-bis(4-pyridylethynyl)benzene **PBP** (**1**): mp=265–266 $^{\circ}\text{C}$ ; 2,5-bis(4-pyridylethynyl)thiophene **PTP** (**2**): mp=210–212 $^{\circ}\text{C}$ ; 4-decyloxybenzoic acid **C<sub>10</sub>OBA** (**3**): Cr 85.1 $^{\circ}\text{C}$  S<sub>X</sub> 96.0 $^{\circ}\text{C}$  S<sub>C</sub> 123.7 $^{\circ}\text{C}$  N 142.4 $^{\circ}\text{C}$  I; 6-decyloxynaphth-2-oic acid **C<sub>10</sub>ONA** (**4**): Cr 104.8 $^{\circ}\text{C}$  Cr' 136.3 $^{\circ}\text{C}$  S<sub>C</sub> 140.5 $^{\circ}\text{C}$  N 175.9 $^{\circ}\text{C}$  I; thiophene-2,5-dicarboxylic acid monodecyl ester **C<sub>10</sub>COOHA** (**5**): mp=104.8 $^{\circ}\text{C}$ ; terephthalic acid monodecyl ester **C<sub>10</sub>COOBA** (**6**): Cr 69.0 $^{\circ}\text{C}$  S<sub>X</sub> 113.3 $^{\circ}\text{C}$  I. <sup>c</sup>Phase transition temperature was observed through optical microscopy.



**Fig. 4** Phase transition temperatures (on heating) of H-bonded trimers **1/3**, **1/4**, **1/5**, **1/6**, **2/3**, **2/4**, **2/5** and **2/6** (molar ratio 1:2).

The *d*-spacing values of the layered S<sub>F</sub>, S<sub>C</sub>, and S<sub>A</sub> phases in H-bonded trimers **1/3**, **1/4**, **1/5**, **1/6**, **2/3**, **2/4**, **2/5** and **2/6** shown in Table 2 are obtained from the powder XRD measurements. Their H-bonded trimeric architectures can be evidenced from the XRD patterns. Since the molecules are orthogonal to the layer in the S<sub>A</sub> phase, the largest *d*-spacing values of the S<sub>A</sub> phases in Table 2 are correlated to the lengths of the supramolecules. Similar to most mesogenic materials, the *d*-spacing values of the S<sub>A</sub> phases in Table 2 decrease as the temperature increases, so the largest *d*-spacing value of the S<sub>A</sub> phases at the lowest temperature in each system is chosen to evaluate its molecular length. The lengths of all components calculated by the molecular modeling are listed as follows: **PBP** (**1**) =  $\sim 15.6 \text{ \AA}$ , **PTP** (**2**) =  $\sim 15.2 \text{ \AA}$ , **C<sub>10</sub>OBA** (**3**) = 19.1/20.6  $\text{ \AA}$ , **C<sub>10</sub>ONA** (**4**) = 21.3/22.8  $\text{ \AA}$ , **C<sub>10</sub>COOHA** (**5**) = 20.7/21.3  $\text{ \AA}$  and **C<sub>10</sub>COOBA** (**6**) = 20.2/21.8  $\text{ \AA}$ ; where the former value is the molecular projection length along the rigid core and the latter value is the fully extended molecular length. The theoretical molecular lengths of H-bonded trimers estimated by the sum of molecular projection lengths of the three H-bonded components along the rigid cores through molecular modeling are also

**Table 2** The largest  $d$ -spacing values of the layered  $S_F$ ,  $S_C$  and  $S_A$  phases in the X-ray diffraction (XRD) measurements of H-bonded trimers **1/3**, **1/4**, **1/5**, **1/6**, **2/3**, **2/4**, **2/5** and **2/6** (molar ratio 1:2) at different temperatures and their theoretical molecular lengths

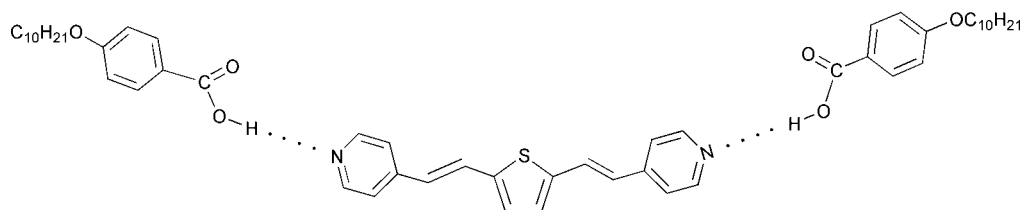
H-bonded trimers	Temperature/ °C <sup>a</sup>	Phase	$d$ -spacing/ Å (XRD)	Theoretical molecular length/Å <sup>c</sup>
<b>1/3</b>	150	$S_F$	50.7	53.8
	175	$S_C$	51.5	
	185	$S_A^b$	51.2	
<b>1/4</b>	150	$S_C$	53.4	58.2
	170	$S_C$	54.3	
	200	$S_A$	55.7	
	210	$S_A$	54.6	
<b>1/5</b>	150	$S_C$	41.5	57.0
	175	$S_C$	43.0	
<b>1/6</b>	130	$S_C$	38.0	56.0
	170	$S_C$	39.2	
<b>2/3</b>	115	$S_A$	52.6	53.4
	120	$S_A$	51.9	
<b>2/4</b>	110	$S_A$	58.9	57.8
	120	$S_A$	57.0	
	130	$S_A$	56.7	
<b>2/5</b>	125	$S_C$	42.4	56.6
	130	$S_C$	42.9	
	135	$S_C$	43.5	
<b>2/6</b>	135	$S_C$	42.1	55.6

<sup>a</sup>All temperatures reported were measured on heating scans. Small temperature deviation from DSC data may occur due to the annealing effect in XRD measurements. <sup>b</sup>The largest  $d$ -spacing values of the  $S_A$  and  $S_C$  phases observed in this H-bonded trimer **1/3** are similar due to a broad and vague transition between the  $S_A$  and  $S_C$  phases. <sup>c</sup>The theoretical molecular lengths of H-bonded trimers are estimated by the sum of molecular projection lengths of the three H-bonded components along the rigid cores through molecular modeling.

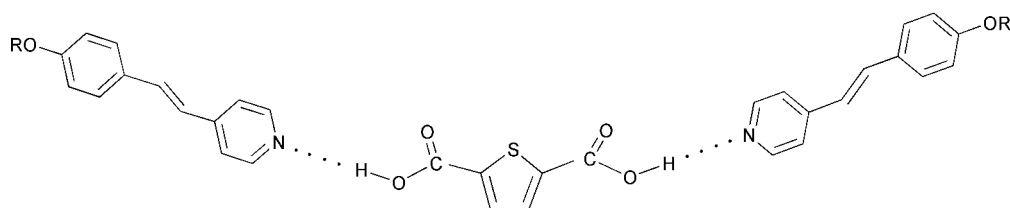
shown in Table 2. According to XRD patterns, H-bonded trimers **1/3**, **1/4**, **2/3** and **2/4** have the largest  $d$ -spacing values of the  $S_A$  phases (Table 2) correlated to their molecular lengths, *i.e.* 51.2 Å (**1/3** at 185 °C), 55.7 Å (**1/4** at 200 °C), 52.6 Å (**2/3** at 115 °C) and 58.9 Å (**2/4** at 110 °C), respectively. Comparing the layer spacing values with the theoretical molecular lengths, *i.e.* 53.8 Å (**1/3**), 58.2 Å (**1/4**), 53.4 Å (**2/3**) and 57.8 Å (**2/4**) (Table 2), all H-bonded trimers, *i.e.* **1/3**, **1/4**, **2/3** and **2/4**, are proved to maintain their H-bonded trimeric architecture. On the basis of the XRD data, H-bonded trimers **1/4** and **2/4** have the largest  $d$ -spacing values (in the  $S_A$  phase), respectively,

in both analogous H-bonded trimeric systems containing acceptors **PBP** (**1**) and **PTP** (**2**), and this result primarily corresponds with the longest molecular length of the naphthalene-based proton donor **4** in all donor moieties. Interestingly, some H-bonded trimers containing the shorter and more kinked core **PTP** (**2**) have larger supramolecular lengths than their analogous H-bonded trimers containing the longer and straighter core **PBP** (**1**). It is noticeable that the H-bonded trimers containing **PBP** (**1**) have shorter  $d$ -spacing values ( $\sim 2.5$  Å shorter) in the  $S_A$  phase than their theoretical molecular lengths in Table 2. This might be explained by the partially kinked structures that are formed to some extent in the H-bonded trimers containing **PBP** (**1**). Also, the theoretical molecular lengths of the other H-bonded trimers **1/5**, **1/6**, **2/5** and **2/6** (with no  $S_A$  phase) are shown to be (see Table 2): 57.0 Å (**1/5**), 56.0 Å (**1/6**), 56.6 Å (**2/5**) and 55.6 Å (**2/6**). Although these H-bonded trimers show no  $S_A$  phase in the XRD measurements from which to judge their molecular lengths, they show much smaller  $d$ -spacing values for the  $S_C$  phase in H-bonded trimers **1/5**, **1/6**, **2/5** and **2/6** (38.0–43.5 Å in  $S_C$ ) in contrast to those in previous H-bonded trimers **1/3** and **1/4** (51.5–54.3 Å in  $S_C$ ). For the **1/3** and **1/4** systems possessing both  $S_C$  and  $S_A$  phases, the  $d$ -spacing values of the  $S_C$  phase (51.5–54.3 Å in  $S_C$ ) are about the same as those of the  $S_A$  phase (51.2–55.7 Å in  $S_A$ ). This indicates that the larger tilt angles of the H-bonded trimers **1/5**, **1/6**, **2/5** and **2/6** in the  $S_C$  phase may be correlated to their donors containing the ester linkage, which might enhance the formation of the  $S_C$  phase with larger tilt angles (about 40–45° tilt angles estimated from Table 2) and thus eliminate the  $S_A$  phase (observed in our earlier comparison of Fig. 4), rather than the ether linkage of the donors in H-bonded trimers **1/3** and **1/4**, which may induce the formation of the  $S_A$  phase instead. The layer spacing values of H-bonded trimers in the  $S_C$  phase seem to be majorly associated with the linkage of the donors and thereafter related to the existence of the  $S_A$  phase, *i.e.* smaller layer spacing values of the  $S_C$  phase in H-bonded trimers possessing no  $S_A$  phase. Generally, the  $d$ -spacing data match the calculated molecular lengths from the molecular modeling, and the XRD results have confirmed their supramolecular structures.

In order to analyze analogous H-bonded trimers, two given comparable H-bonded trimers **2/3** and  $(C_nPS)_2$ -THDA (where  $n=10$ ), in which both possess five aromatic rings (two benzene and pyridine rings on both sides, and one thiophene ring in the center), two  $-C=C-$  linkages, and two carboxylic acid H-bonds but owning different sequences in the structural combination, are compared and demonstrated below.



H-bonded trimers **2/3**

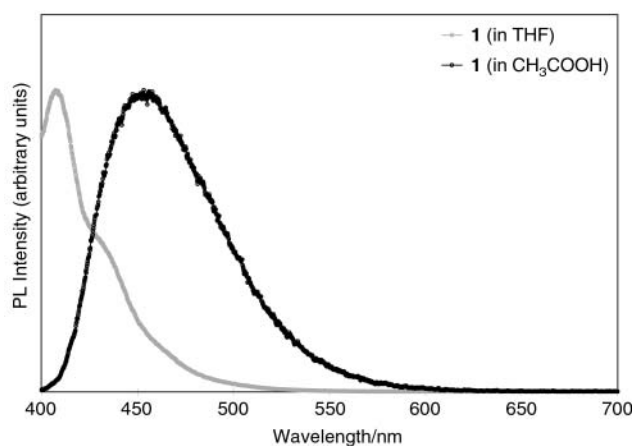


$R=C_nH_{2n+1}$ , where  $n=8, 10$  and  $12$ .

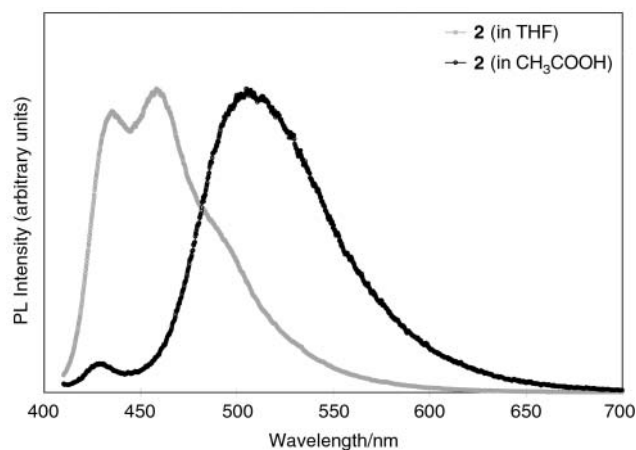
H-bonded trimers  $(C_nPS)_2$ -THDA

With respect to the mesogenic properties and XRD results of  $(C_nPS)_2$ -THDA (where  $n=8$  and  $12$ ), which were reported earlier,<sup>16</sup>  $(C_{12}PS)_2$ -THDA has the following thermal properties: Cr 69.4 °C Cr' 140.3 °C S<sub>A</sub> 175.0 °C N 188.8 °C I (on heating) and  $(C_8PS)_2$ -THDA has similar mesogenic properties with S<sub>A</sub> and N phases, and the largest  $d$ -spacing values of the S<sub>A</sub> phase (from XRD) are around 54–55 Å in both H-bonded trimers  $(C_nPS)_2$ -THDA ( $n=8$  and  $12$ ). Thus,  $(C_{10}PS)_2$ -THDA can be predicted to have both S<sub>A</sub> and N phases, which are not possessed in both acceptor and donor moieties ( $C_{10}PS$  and THDA), and the largest  $d$ -spacing value of 54–55 Å in the S<sub>A</sub> phase can be predicted as well. In contrast to analogous  $(C_{10}PS)_2$ -THDA, the H-bonded trimer **2/3** has a broader S<sub>A</sub> phase (112.7–186.5 °C on heating) but no N phase. Though the donor moiety of **2/3**, *i.e.* donor **3**, possesses both S<sub>C</sub> and N phases, H-bonded trimer **2/3** has completely different mesomorphism, *i.e.* reveals a S<sub>A</sub> phase only. Besides, **2/3** has a similarly large  $d$ -spacing value of 52.6 Å (in the S<sub>A</sub> phase) to that of analogous  $(C_{10}PS)_2$ -THDA (around 54–55 Å), that suggests these two analogous H-bonded trimers **2/3** and  $(C_nPS)_2$ -THDA may have similar configurations of H-bonded architecture.

The conjugated bis-pyridyl compounds (**1** and **2**) in these H-bonded trimers possess photoluminescent (PL) properties and they can be used as proton acceptors to form supramolecular structures in this study. According to our previous work,<sup>21</sup> the photoluminescent bis-pyridyl compounds **1** and **2** show different emission peaks depending on their central cores (benzene in **1** and thiophene in **2**), and bis-pyridyl compound **2** containing the thiophene unit has larger  $\lambda_{\max}$  than that of bis-pyridyl compound **1** due to the smaller energy gap (lower oxidation potential) of the thiophene-based structure in compound **2**. We know that pH values of aqueous solutions may affect PL properties of polyelectrolytes containing pyridine; hence, hydrogen bonds in these supramolecular liquid crystals may have a critical influence on the PL properties of the conjugated bis-pyridyl compounds. Before the H-bonded effects on photoluminescent supramolecules in solid films have been surveyed, solution forms of photoluminescent bis-pyridyl acceptors (**1** and **2**) in different pH values of solvent, *i.e.* THF and CH<sub>3</sub>COOH, are investigated first. The PL spectra of **PBP (1)** and **PTP (2)** in solutions of THF and CH<sub>3</sub>COOH are shown in Fig. 5 and Fig. 6, and their emission peaks of  $\lambda_{\max}$  of solutions and solid films (reported previously)<sup>21</sup> are listed in Table 3. The exciting wavelength of the incident beam  $\lambda_{\text{ex}}$  is 380 nm. In comparison with **PBP (1)** and **PTP (2)** in a solution of THF, the emission peaks of  $\lambda_{\max}$  of the PL spectra in the solution of CH<sub>3</sub>COOH have approximately 50 nm red shifts (*i.e.* from 407 nm to 453 nm in **1** and from 458 nm to 505 nm in **2**) due to its smaller solvent pH value in



**Fig. 5** Photoluminescence spectra of 1,4-bis(4-pyridylethenyl)benzene **PBP (1)** in solutions of THF and CH<sub>3</sub>COOH.



**Fig. 6** Photoluminescence spectra of 2,5-bis(4-pyridylethenyl)thiophene **PTP (2)** in solutions of THF and CH<sub>3</sub>COOH.

CH<sub>3</sub>COOH. The  $pK_a$  value of the solvent CH<sub>3</sub>COOH is 4.07, so the proton donor effect in CH<sub>3</sub>COOH solvent with higher acidity is stronger than that in THF solvent with a more neutral pH value. Similar red shifts (36–96 nm) also occur in their pure solid films, which might be due to the formation of excimers originated from  $\pi$ - $\pi$  stacking and molecular aggregation of conjugated bis-pyridyl compounds (**1** and **2**) in the solid state. Similar to solution approaches, the H-bonded effects on the photoluminescence of these supramolecular liquid crystals in the solid form are conceivable if we consider the supramolecular systems as solid solutions (non-photoluminescent donors as solvents) with different degrees of hydrogen-bonding. The PL spectra of photoluminescent **PBP (1)** and **PTP (2)** in their supramolecular structures (in solid films), *i.e.* H-bonded trimers **1/3**, **1/4**, **1/5**, **1/6**, **2/3**, **2/4**, **2/5** and **2/6** (1:2 molar ratio) are shown in Fig. 7 and Fig. 8, and their emission peaks of  $\lambda_{\max}$  in the PL spectra and the  $pK_a$  values of the pure proton donors (**3–6**) are listed in Table 4. The proton donors (**3–6**) in the H-bonded trimers do not have photoluminescent properties due to their lack of conjugated structures, and they only offer the solid solvent environment with different  $pK_a$  values (**C<sub>10</sub>OBA (3)**:  $pK_a=4.21$ ; **C<sub>10</sub>ONA (4)**:  $pK_a=4.17$ ; **C<sub>10</sub>COOHA (5)**:  $pK_a=3.49$ ; **C<sub>10</sub>COOBA (6)**:  $pK_a=4.21$ )<sup>26</sup> thus giving different degrees of H-bonding for the photoluminescent acceptor cores (**1** and **2**), *i.e.* different electron density caused by protonation of distinct solid donors. Consequently, the emission peaks of the H-bonded trimers containing the photoluminescent bis-pyridyl cores (**1** and **2**) in Table 4 can generate 30–40 nm difference of emission in  $\lambda_{\max}$  depending on the non-photoluminescent proton donors. On the basis of our findings, the PL spectra of these H-bonded trimers indicate the largest red shift is observed in both H-bonded trimers **1/5** and **2/5** containing thiophene donor **5** possibly due to it having the smallest  $pK_a$  value and the largest degree of H-bonding

**Table 3** The emission peaks,  $\lambda_{\max}$  (nm), of photoluminescence spectra<sup>a</sup> of 1,4-bis(4-pyridylethenyl)benzene **PBP (1)** and 2,5-bis(4-pyridylethenyl)thiophene **PTP (2)** in the solutions (THF and CH<sub>3</sub>COOH)<sup>b</sup> and solid films

Acceptor	$\lambda_{\max}$ /nm
<b>1</b> (in THF)	407
<b>1</b> (in CH <sub>3</sub> COOH)	453
<b>1</b> (in solid film)	443
<b>2</b> (in THF)	458
<b>2</b> (in CH <sub>3</sub> COOH)	505
<b>2</b> (in solid film)	554

<sup>a</sup>The exciting wavelength of the incident beam,  $\lambda_{\text{ex}}$ , is 380 nm. <sup>b</sup>The concentrations of solutions in THF and CH<sub>3</sub>COOH are less than  $5 \times 10^{-6}$  M and the  $pK_a$  value of CH<sub>3</sub>COOH is 4.07.

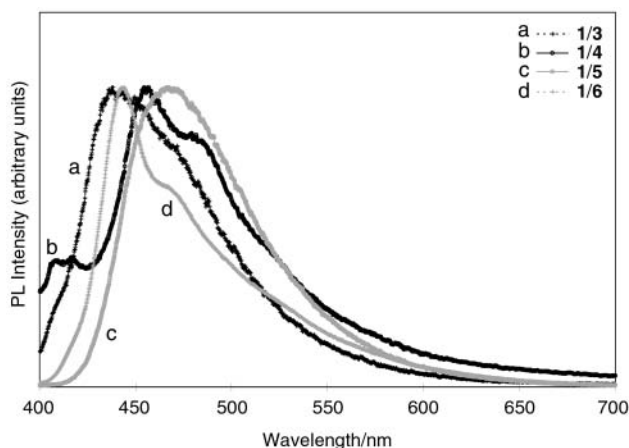


Fig. 7 Photoluminescence spectra of H-bonded trimers (in solid films) 1/3, 1/4, 1/5 and 1/6 (molar ratio 1:2) containing photoluminescent core 1,4-bis(4-pyridylethenyl)benzene PBP (1).

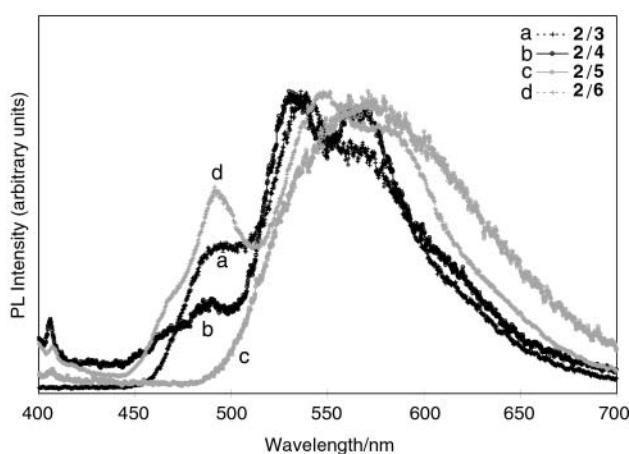


Fig. 8 Photoluminescence spectra of H-bonded trimers (in solid films) 2/3, 2/4, 2/5 and 2/6 (molar ratio 1:2) containing photoluminescent core 2,5-bis(4-pyridylethenyl)thiophene PTP (2).

compared with the analogous systems. Similar results have been explained in the literature by the red shift emission of polyelectrolytes that occurs at lower pH values in the aqueous form due to the protonation of the pyridine nitrogen. Indeed, the results demonstrate that a red shift occurs in these H-bonded trimers when proton donors with smaller  $pK_a$  values are H-bonded to the supramolecules. Therefore, the  $\lambda_{max}$  values, i.e. the colors, of the photoluminescence in the supramolecular systems can be tuned not only by adjusting the photoluminescent cores but also by changing between the different  $pK_a$  values of the non-photoluminescent proton donors.

In another aspect, by adding proton donors to let the photoluminescent moieties possess liquid crystalline properties in the H-bonded structures, they can be aligned by heating of the mesogenic phase in the rubbing cells so as to generate linearly polarized light during the PL process. One proof of this prospect has been done by injection of H-bonded complex 2/4 into an antiparallel rubbing cell (with 9  $\mu\text{m}$  cell gap) and heating up to 120  $^{\circ}\text{C}$  (in the  $S_A$  phase) to align the sample. By irradiation of UV light (with exciting wavelength of  $\lambda_{ex} = 365$  nm) on the aligned  $S_A$  phase at 120  $^{\circ}\text{C}$ , polarized emission of PL is observed with a polarizer parallel and perpendicular to the rubbing direction and the polarization intensity ratio is around 1.82 (as shown in Fig. 9). After cooling to room temperature, similar polarized photoluminescent properties are still sustained in the solid state, which means the alignment is somewhat maintained even after crystallization. A more

**Table 4** The emission peaks,  $\lambda_{max}$  (nm), of photoluminescence spectra<sup>a</sup> of H-bonded trimers (in solid films) 1/3, 1/4, 1/5, 1/6, 2/3, 2/4, 2/5 and 2/6 (molar ratio 1:2) containing photoluminescent cores 1,4-bis(4-pyridylethenyl)benzene PBP (1) and 2,5-bis(4-pyridylethenyl)thiophene PTP (2)<sup>b</sup>

Trimer	$\lambda_{max}/\text{nm}$
1/3 (PBP/C <sub>10</sub> OBA)	438
1/4 (PBP/C <sub>10</sub> ONA)	457
1/5 (PBP/C <sub>10</sub> COOHA)	467
1/6 (PBP/C <sub>10</sub> COOBA)	444
2/3 (PTP/C <sub>10</sub> OBA)	537
2/4 (PTP/C <sub>10</sub> ONA)	530
2/5 (PTP/C <sub>10</sub> COOHA)	571
2/6 (PTP/C <sub>10</sub> COOBA)	551

<sup>a</sup>The exciting wavelength of the incident beam,  $\lambda_{ex}$ , is 380 nm. <sup>b</sup> $pK_a$  values of proton donors are as follows: 4-decyloxybenzoic acid C<sub>10</sub>OBA (3):  $pK_a = 4.21$ . 6-Decyloxy-2-naphthoic acid C<sub>10</sub>ONA (4):  $pK_a = 4.17$ . Thiophene-2,5-dicarboxylic acid monodecyl ester C<sub>10</sub>COOHA (5):  $pK_a = 3.49$ . Terephthalic acid monodecyl ester C<sub>10</sub>COOBA (6)  $pK_a = 4.21$ .

detailed study will be performed in the future. Accordingly, these results also show the feasibility of production of linearly polarized light from supramolecular design by using the combination of liquid crystalline and photoluminescent properties.

Overall, distinct supramolecular liquid crystalline materials can be generated by complexation of different complementary donors and acceptors. The supramolecular architecture and novel mesomorphic properties are confirmed by polarizing optical microscopy, DSC, and powder XRD experiments in this study. PL properties are also investigated to realize the H-bonded effects on these supramolecular trimers. Nevertheless, the H-bonded trimers could not be utilized for LED applications due to the poor film-forming quality of the small molecules. In order to solve this problem, we have surveyed new H-bonded polymer systems containing photoluminescent bis-pyridyl acceptors H-bonded to polymeric donors, and it leads to high quality films of supramolecular LED polymers. Related results will be published later. Consequently, H-bonded photoluminescent materials possessing liquid crystalline properties may find practical use in the future.

## Conclusions

In conclusion, we can easily adjust the physical properties of the H-bonded trimers by tuning the H-bonded donors and acceptors in the complexes. Unique mesomorphic properties may occur in these supramolecular structures. Similar to traditional molecular structures containing naphthalene, benzene, and thiophene units, the H-bonded trimeric structures

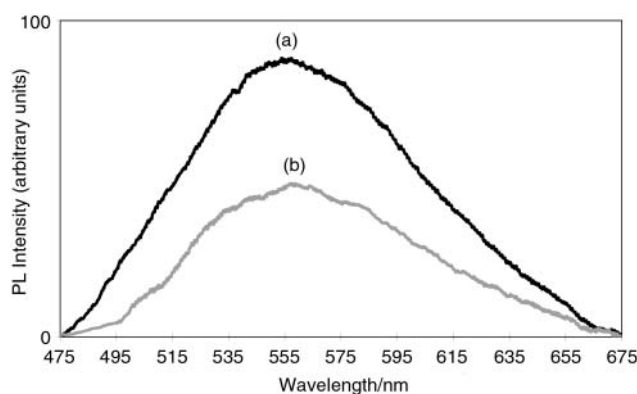


Fig. 9 Photoluminescence spectra of 2/4 at 120  $^{\circ}\text{C}$  ( $S_A$  phase) with the polarizer (a) parallel and (b) perpendicular to the rubbing direction and the polarization intensity ratio is around 1.82.

have phase transition temperatures related to their nonlinearity and rigidity. In addition, the emission peaks of the photoluminescent cores containing bis-pyridyl groups can be adjusted by their surrounding non-photoluminescent proton donors. A red shift is expected in the H-bonded structures where proton donors with smaller  $pK_a$  values are H-bonded to the photoluminescent cores. Therefore, we can control the mesomorphic and photoluminescent properties effectively by these concepts in supramolecular architecture.

## Acknowledgements

The Department of Materials Science and Engineering at National Chiao Tung University, Institute of Chemistry at Academia Sinica, China Petroleum Corporation (Grant No. NSC 88-CPC-M-001-007) and the National Science Council (Grant No. NSC 89-2113-M-001-045) of the Republic of China are acknowledged for the financial support of this project.

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