Available online at www.sciencedirect.com
ScienceDirect
Spectrochimica Acta Part A 66 (2007) 1300–1306
SPECTROCHIMICA ACTA PART A
www.elsevier.com/locate/saa

Optical behaviors of conjugated-chain compounds containing benzene and furan units

Wen-Long Pan, Ji-Guo Song, Yong Chen, Yi-Qian Wan, Hua-Can Song *

School of Chemistry and Chemical Engineering, Sun yat-Sen University, Guangzhou 510275, PR China

Received 18 April 2006; accepted 9 May 2006

Abstract

Thirteen conjugated-chain compounds which contain benzene and furan units were prepared, their optical behaviors, including UV–vis absorption coefficient (ε), absorption wavelengths (λ_a), fluorescence emission wavelengths (λ_e), and quantum yields (Φ) were measured. Meanwhile, their LUMO and HOMO energy were determined by cyclic voltammetry and their second-order polarizations (β_{xxx}) values were determined by solvatochromic method, respectively. The results showed that this kind of compounds possess a shorter λ_a (320–365 nm) and performance a higher Φ values, especially for **2aa**, **2ab**, **2ac** and **2bb**, their Φ values are all more than 90%. These compounds, except **2db**, showed a higher β_{xxx} values in DMSO, especially for **2dc** (75.77×10^{-30} m^5 C^{-1}) and **2dd** (83.32×10^{-30} m^5 C^{-1}), than that 10-methyl-acridone (6.578×10^{-30} m^5 C^{-1}) or 10-benzylacridone (6.845×10^{-30} m^5 C^{-1}) in DMSO did, and second harmonic generation value of 10-methylacridone and 10-benzylacridone in powder are, respectively, 1.381 and 1.861 times of that value of urea. The β_{xxx} values and Φ values determined for these compounds in this work were lower than these values which were desired in the original work, this phenomena was explained from their molecular structures. This work confirmed that as these compounds performance shorter λ_a and higher Φ values, they could be good blue-color optical materials for some fields, such as OLED materials, two-photo absorption materials, fluorescent dyes.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Conjugated compound; Trisbustituted-furan; Synthesis; Optical behavior

1. Introduction

It has attracted a tremendous amount of recent attention to synthesize and investigate the optical behaviors of conjugated organic materials and many remarkable research results were obtained recently in many fields, such as in organic second-order nonlinear optical (NLO) materials [1–3], in two-photon absorption materials [4–6] and in organic light-emitting device (OLED) [7–11] materials. There are a lot of reports about the conjugated-chain compounds containing benzene and thiophene units [12–20] which could show a good photoluminescence property and it was found several papers about the conjugated-chain compounds containing benzene and furan units could perform a good optical property [8c,21–24]. However, there is very little of the reports about the fluorescence-emitting behaviors and second-order polarizations of the conjugated-chain compounds containing benzene and furan units. Therefore, based on our previous work [25–28], we wish to report herein the preparation of a series of conjugated-chain compounds which contain benzene and furan units and their optical behaviors, including UV–vis absorption coefficient (ε), absorption wavelengths (λ_a), fluorescent emitting wavelengths (λ_e), quantum yields (Φ), LUMO energy and HOMO energy and second-order polarization (β_{xxx}) values. The synthetic method and structures for these compounds were in the following (Fig. 1).

2. Results and discussion

2.1. The preparation of samples

According to Refs. [23,25], a series of conjugated-chain compounds which contain benzene and furan fragments were prepared in our laboratory, the synthetic method and structures of trisbustituted-furan derivatives were showed in Fig. 1. In order to prepare 1-hexynyl (or phenylacetylenyl) aromatic alcohol, 1-hexynyllithium (or phenylacetylenyllithium) was employed. As a lower temperature (under −78 °C) must be necessary for the preparation of alkynyllithium by the reaction of butyllithium

---

* Corresponding author. Tel.: +86 20 84110918; fax: +86 20 84112245.
E-mail address: cedc19@zsu.edu.cn (H.-C. Song).

1386-1425/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2006.05.035

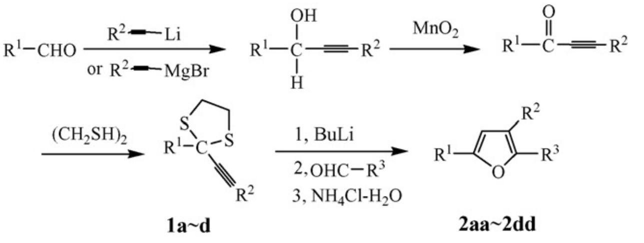

Fig. 1. The synthetic method and structures of trisbustituted-furan derivatives. **1a**, R^1 = 4-methoxycarbonylphenyl, R^2 = n-C_4H_9; **1b**, R^1 = 4-biphenyl, R^2 = phenyl; **1c**, R^1 = 4-methoxyphenyl, R^2 = phenyl; **1d**, R^1 = 2-naphthyl, R^2 = phenyl. **2aa**, R^3 = 4-phenyl; **2ab**, R^3 = 4-trifluoromethylphenyl; **2ac**, R^3 = 2,4-dimethoxyphenyl; **2ba**, R^3 = 2,4-dimethoxyphenyl; **2bb**, R^3 = 4-fluorophenyl; **2bc**, R^3 = 4-cyanophenyl; **2ca**, R^3 = 4-cyanophenyl; **2cb**, R^3 = 4-fluorophenyl; **2cc**, R^3 = 4-hydroxyphenyl; **2da**, R^3 = 4-fluorophenyl; **2db**, R^3 = 2,4-dimethoxyphenyl; **2dc**, R^3 = 4-hydroxyphenyl; **2dd**, R^3 = 4-acryloyloxy.

with 1-hexyne (or phenylacetylene), the reaction of alkynyllithium with methylmagnesium iodide at 0–10 °C was tried and a good yield for the reaction was obtained.

After aromatic aldehyde was added into the mixture of dithiaacetal and butyllithium, it is better to keep this resulting mixture for 40 min under −78 °C, in order to get a high yield for trisubstituted-furan compounds. If the reaction time was prolonged for 60–80 min, the yield would become lower; if after the addition of aldehyde the mixture was lad up at the room temperature and let the temperature of the mixture go up by itself, the yield became very low and even the desired product could not be isolated.

In order to get 4-acryloyloxyphenylfuran (**2dd**) for polymerization, synthetic routes 1–3 for 4-hydroxyphenyl furan (**2dc**) were tried, respectively (Fig. 2). By routes 2 and 3 a good result could be obtained, but a lower yield by route 1 was obtained, as the yield for demethylation was very low.

2.2. Quantum yields

The Φ values for thirteen trisubstituted-furan derivatives were determined by comparing method, using coumarin as a standard sample and its Φ value is 0.99 in ethyl acetate [29]. The results were listed in Table 1.

Table 1
The quantum yield of compounds **2aa**–**2dd** in ethyl acetate

Sample	Φ (%)
2aa	97
2ab	91
2ac	101
2ba	81
2bb	93
2bc	78
2ca	89
2cb	66
2cc	71
2da	72
2db	79
2dc	70
2dd	66

It is found from Table 1 that this series of trisubstituted-furan derivatives possess a strong fluorescence emitting ability, all of their Φ values are more than 66%, especially for **2aa**, **2ab**, **2ac**, **2bb**, their Φ values are all more than 90%, and for **2ba** and **2ca**, their Φ values are all more than 80%. Compared with the previously reported quantum yield values [24], it is confirmed that the Φ values of compounds could be increased by changing their structures.

By comparison with the structures and Φ values, it is found generally that those trisubstituted-furan derivatives in which there is an n-butyl group in three-position possess a stronger fluorescence emitting ability than that in which there is a phenyl group in three-position do. This is because that a phenyl group in three-position of furan-derivative molecules has a stronger tendency as space factor to twist the plane which furan ring and the other phenyl ring (or aromatic ring) are in at the same time, which would destroy the rigid structure in which furan ring and the other phenyl ring (or aromatic ring) should keep, compared with an n-butyl group in three-position of the same furan-derivative molecules.

2.3. LUMO and HOMO

According to Ref. [30], the determination for HOMO and LUMO energy of the samples **2aa**–**2dd** were finished by cyclic voltammetry (CV) in 0.1 M solution of TBAP in acetonitrile, platinum electrode and SCE were used as the working electrode and the reference electrode, respectively, the scan rate was 100 mV s^{-1}. The oxidation potential (E_{pa}), reduction potential (E_{pc}), HOMO energy, LUMO energy and band gaps were shown in Table 2.

The redox properties of the furan compounds could be ascribed to reduction and oxidation occurring on the furan backbone. The conjugation degrees of the aromatic π-system could

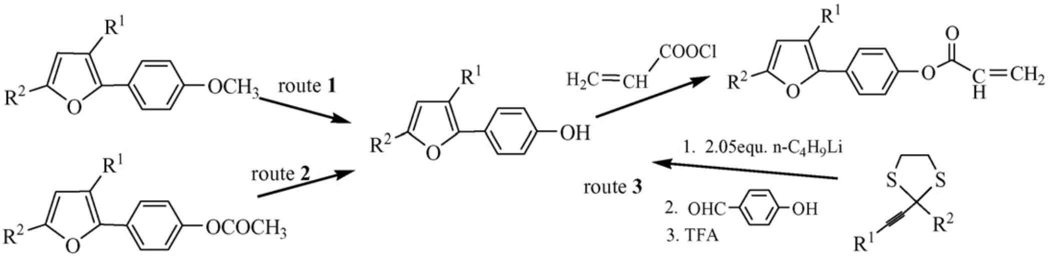

Fig. 2. The synthetic route 1–3 for 4-hydroxyphenyl furan (2dc)

Table 2
HOMO and LUMO (electrochemical data) of compounds **2aa**–**2dd**

Sample	E_{pa} (V)	HOMO (eV)	E_{pc} (V)	LUMO (eV)	E_{gap} (eV)
2aa	0.90	5.64			
2ab	1.03	5.77	−1.75	2.99	2.78
2ac	0.96	5.70	−1.87	2.87	2.83
2ba	0.97	5.71	−1.66	3.08	2.63
2bb	1.14	5.88			
2bc	1.05	5.79			
2ca	0.97	5.71			
2cc	0.92	5.66			
2da	0.84	5.58			
2db	0.82	5.56			
2dc	0.87	5.61	−1.84	2.90	2.71
2dd	1.24	5.98	−1.79	2.95	3.03

produce a significant perturbation on the properties of molecular orbits, which would influence the energy gap.

It is found from Table 2 that in this condition the oxidation and reduction peaks could be obtained for **2ab**, **2ac**, **2ba**, **2dc** and **2dd**, which means that the electrochemistry-behavior was reversible in this situation for these samples. But the oxidation and reduction peaks were not obtained for **2aa**, **2bb**, **2bc**, **2ca**, **2cc**, **2da** and **2db**, which indicates that the electrochemistry-behavior was irreversible for these samples. The reason for this phenomenon was suggested that the ionic species were either very stable or transformed into the electro-inactive species. It is likely that the radical anion obtained after the reduction (or oxidation) was protonated in solution (CH_3CN), which may contain a trace amount of water.

The presence of the phenyl group obviously made the electrochemical reduction and oxidation much easier, as reduction potentials were increased from −2.6 to −2.2 V, and oxidation potentials were decreased from 1.24 to 0.82 V.

Unfortunately the LUMO energy could not be obtained for several compounds, since their reduction potentials were out of the solvent window. The energy level of the HOMO in respect to vacuum was, therefore, compatible with the excellent hole-transporting materials such as TPD (5.60 eV) or NPB (5.40 eV). These furan derivatives are blue light-emitting compounds with high PL in solution and thus showed a great potential as optoelectronic materials. Further electrochemical and solid-state studies were under way and will be reported in due course.

2.4. Second-order polarizations

According to Eqs. (1)–(5) [25–28] and based on the solvatochromic method which was reported in our previous work, the values of β_{xxx} were determined in five solvents. From CRC Handbook of Chemistry and Physics Data, 58th, it was found that the dielectric constant for these five solvents, DMF, DMSO, 1,2-dichloro-ethane, ethyl acetate and dichloromethane is, respectively, 37.00, 49.00, 10.45, 6.02 and 9.10. All the data correlated with this calculation were listed in Tables 3–8.

$$\beta_{xxx} = \frac{1.5h^{-2}\mu_{eg}^{2}(\mu_{e}-\mu_{g})\omega_{eg}^{2}}{(\omega_{eg}^{2}-\omega^{2})(\omega_{eg}^{2}-4\omega^{2})} \tag{1}$$

$$\text{area} = \frac{2\pi\omega_{eg}N_{0}n\mu_{eg}^{2}M}{3(2.303)\varepsilon_{0}ch} \tag{2}$$

Table 3
The calculated data of M, B, α, and $\mu_e - \mu_g$ of the samples

	Samples										
	2aa	**2ab**	**2ba**	**2bb**	**2ca**	**2cb**	**2cc**	**2da**	**2db**	**2dc**	**2dd**
M	352	402	432	371	351	344	342	364	406	362	416
B	3471.4	1883.7	2022.2	614.4	2291.8	2985	1302	915.8	677.9	3583.6	2699.7
α	1.5071	1.5486	1.842	1.7184	1.6037	1.5238	1.5325	1.5398	1.6785	1.5721	1.9194
$\mu_e - \mu_g$ ($\times 10^{-30}$ cm)	57.738	32.193	41.108	11.652	40.561	50.198	22.020	15.562	12.557	62.174	57.186

Table 4
Concentration,λ_a, ε, λ_e, H, $r_{1/2}$, Stokes shift, μ_{eg}, ω_{eg} and β_{xxx} in DMSO

	Samples										
	2aa	**2ab**	**2ba**	**2bb**	**2ca**	**2cb**	**2cc**	**2da**	**2db**	**2dc**	**2dd**
Concentration ($\times 10^{-6}$ mol/L)	2.890	2.488	2.315	2.695	2.849	2.907	2.924	2.747	2.463	2.762	2.404
λ_a (nm)	348	349	327	343	364	344	337	343	337	345	345
ε ($\times 10^{7}$ cm^2 mol^{-1})	4.400	4.744	8.165	6.826	3.019	2.821	4.480	4.623	2.923	4.706	5.366
λ_e (nm)	436	422	443	408	462	409	415	404	438	441	434
H	0.125	0.118	0.189	0.184	0.086	0.082	0.131	0.127	0.072	0.130	0.129
$r_{1/2}$ (cm^{-1})	4364.5	4326.5	3458.7	3749.4	4617.4	2038.6	3183.2	4173.0	3009.2	4906.5	5132.3
Stokes shift (nm^{-1})	5799.9	4956.6	8007.7	4687.3	5865.3	4619.9	5577.2	4402.0	6842.5	6309.8	5944.0
μ_{eg} ($\times 10^{-30}$ cm)	38.03	39.45	44.79	43.69	33.16	20.69	32.33	37.92	25.38	41.53	45.40
ω_{eg} (cm^{-1})	28735.6	28653.3	30581.0	29154.5	27472.5	29069.8	29673.6	29154.5	29673.6	28985.5	28985.5
β_{xxx} ($\times 10^{-30}$ m^5 C^{-1})	60.95	36.96	48.20	15.31	38.53	15.03	14.94	15.48	5.25	75.77	83.32

Table 5
Concentration, λ_a, ε, λ_e, H, $r_{1/2}$, Stokes shift, μ_{eg}, ω_{eg} and β_{xxx} in DMF

	Samples										
	2aa	**2ab**	**2ba**	**2bb**	**2ca**	**2cb**	**2cc**	**2da**	**2db**	**2dc**	**2dd**
Concentration ($\times 10^{-6}$ mol/L)	2.890	2.488	2.315	2.695	2.849	2.907	2.924	2.747	2.463	2.762	2.404
λ_a (nm)	345	352	330	338	363	324	328	333	328	335	336
ε ($\times 10^{7}$ cm^2 mol^{-1})	4.400	4.744	8.165	6.826	3.019	2.821	4.480	4.623	2.923	4.706	5.366
λ_e (nm)	433	415	442	405	456	402	414	400	434	434	435
H	0.090	0.107	0.085	0.140	0.091	0.096	0.113	0.121	0.096	0.100	0.096
$r_{1/2}$ (cm^{-1})	4452.1	3650.9	4818.1	4539.7	4399.3	4990.8	5109.7	5519.6	5420.0	6495.9	6047.9
Stokes shift (nm^{-1})	5890.8	4353.1	7678.6	4938.3	5618.4	5988.6	6333.2	5030.0	7446.3	6809.3	6773.4
μ_{eg} ($\times 10^{-30}$ cm)	33.10	35.25	36.23	42.32	33.91	34.65	38.16	42.72	39.47	42.07	42.72
ω_{eg} (cm^{-1})	28985.5	28409.1	30303.0	29585.8	27548.2	30864.2	30487.8	30030.0	30487.8	29850.7	29761.9
β_{xxx} ($\times 10^{-30}$ m^5 C^{-1})	44.70	30.31	32.54	13.62	40.06	34.14	18.94	17.67	11.55	69.93	67.03

Table 6
Concentration, λ_a, ε, λ_e, H, $r_{1/2}$, Stokes shift, μ_{eg}, ω_{eg} and β_{xxx} in $ClCH_2CH_2Cl$

	Samples										
	2aa	**2ab**	**2ba**	**2bb**	**2ca**	**2cb**	**2cc**	**2da**	**2db**	**2dc**	**2dd**
Concentration ($\times 10^{-6}$ mol/L)	2.890	2.488	2.315	2.695	2.849	2.907	2.924	2.747	2.463	2.762	2.404
λ_a (nm)	349	351	327	341	365	320	324	341	325	341	342
ε ($\times 10^{7}$ cm^2 mol^{-1})	4.400	4.744	8.165	6.826	3.019	2.821	4.480	4.623	2.923	4.706	5.366
λ_e (nm)	423	408	435	405	446	395	401	403	431	422	414
H	0.081	0.052	0.058	0.092	0.076	0.061	0.059	0.088	0.0797	0.087	0.048
$r_{1/2}$ (cm^{-1})	3830.7	3656.8	5852.3	3841.5	3914.3	5779.6	5310.7	4450.5	6818.8	5146.6	4656.8
Stokes shift (nm^{-1})	5012.6	4634.2	7592.5	4634.2	5013.3	5982.4	5974.2	4511.6	7567.3	5671.9	5128.0
μ_{eg} ($\times 10^{-30}$ cm)	29.04	24.31	32.65	31.51	29.05	29.32	27.71	32.80	39.93	34.97	26.57
ω_{eg} (cm^{-1})	28653.3	28490.0	30581.0	29325.5	27397.3	31250.0	30864.2	29325.5	30769.2	29325.5	29239.8
β_{xxx} ($\times 10^{-30}$ m^5 C^{-1})	35.91	14.26	25.60	7.83	29.90	23.32	9.53	11.34	11.45	51.21	27.48

Table 7
Concentration, λ_a, ε, λ_e, H, $r_{1/2}$, Stokes shift, μ_{eg}, ω_{eg} and β_{xxx} in EtOAc

	Samples										
	2aa	**2ab**	**2ba**	**2bb**	**2ca**	**2cb**	**2cc**	**2da**	**2db**	**2dc**	**2dd**
Concentration ($\times 10^{-6}$ mol/L)	2.890	2.488	2.315	2.695	2.849	2.907	2.924	2.747	2.463	2.762	2.404
λ_a (nm)	346	346	327	336	362	318	323	336	326	339	331
ε ($\times 10^{7}$ cm^2 mol^{-1})	4.400	4.744	8.165	6.826	3.019	2.821	4.480	4.623	2.923	4.706	5.366
λ_e (nm)	412	403	423	400		394	399	396	414	415	412
H	0.070	0.129	0.052	0.115	0.061	0.071	0.076	0.107	0.075	0.057	0.035
$r_{1/2}$ (cm^{-1})	3759.9	3953.2	4305.8	4229.4	3578.6	5635.7	5358.4	4608.9	2835.8	5450.5	5912.2
Stokes shift (nm^{-1})	4671.7	4087.8	2803.0	4761.9	4935.2	6065.8	5897.1	4509.4	6520.2	5445.7	5939.6
μ_{eg} ($\times 10^{-30}$ cm)	27.39	40.79	27.87	37.73	25.46	32.05	32.45	37.62	27.32	29.95	25.93
ω_{eg} (cm^{-1})	28901.7	28901.7	30581.0	29761.9	27624.3	31446.5	30959.8	29761.9	30674.8	29498.5	30211.5
β_{xxx} ($\times 10^{-30}$ m^5 c^{-1})	30.78	38.26	18.56	10.66	22.22	27.43	12.99	14.15	5.42	36.79	23.44

Table 8
Concentration, λ_a, ε, λ_e, H, $r_{1/2}$, Stokes shift, μ_{eg}, ω_{eg} and β_{xxx} in CH_2Cl_2

	Samples										
	2aa	**2ab**	**2ba**	**2bb**	**2ca**	**2cb**	**2cc**	**2da**	**2db**	**2dc**	**2dd**
Concentration ($\times 10^{-6}$ mol/L)	2.890	2.488	2.315	2.695	2.849	2.907	2.924	2.747	2.463	2.762	2.404
λ_a (nm)	323	351	326	341	360	322	325	342	326	342	347
ε ($\times 10^{7}$ cm^2 mol^{-1})	4.400	4.744	8.165	6.826	3.019	2.821	4.480	4.623	2.923	4.706	5.366
λ_e (nm)	426	410	432	406	445	398	402	399	431	419	417
H	0.127	0.116	0.112	0.125	0.169	0.126	0.158	0.114	0.103	0.088	0.108
$r_{1/2}$ (cm^{-1})	3233.0	3646.7	6024.7	4080.8	3472.2	6186.0	6139.4	4173.0		4889.0	3811.7
Stokes shift (nm^{-1})	4894.6	4099.8	7526.7	4695.0	5305.9	5978.6	5941.0	4219.9		5373.4	4879.2
μ_{eg} ($\times 10^{-30}$ cm)	33.85	36.69	46.25	38.13	40.92	44.07	49.27	36.45	45.14	34.71	36.49
ω_{eg} (cm^{-1})	30959.8	28490.0	30674.8	29325.5	27777.7	31055.9	30769.2	29239.8	30674.8	29239.8	28818.4
β_{xxx} ($\times 10^{-30}$ m^5 C^{-1})	50.69	32.66	50.84	11.47	56.47	53.79	30.43	14.08	14.80	51.29	54.69

$$
\begin{aligned}
\mu_{\mathrm{eg}}^2 &= \frac{6.909 H r_{1/2} \varepsilon_0 c h}{2\pi \omega_{\mathrm{eg}} N_0 n M} \\
&= \frac{32.11662 \times 10^{-61} H r_{1/2}}{n M \omega_{\mathrm{eg}}}\,(\mathrm{mol\,C^2\,m^{-1}}) \\
&= \frac{3.211662 \times 10^{-58} H r_{1/2} m}{n \omega_{\mathrm{eg}}}\,(\mathrm{C^2 m^2}) \qquad (3)
\end{aligned}
$$

$$
\begin{aligned}
V_{\mathrm{a}} - V_{\mathrm{f}} &= A + B(BK), \qquad B = \frac{2(\mu_{\mathrm{e}} - \mu_{\mathrm{g}})^2}{hc\alpha^3}, \\
BK &= \left[\frac{D-1}{2D+1} - \frac{n^2-1}{2n^2-1}\right] \text{¡}\hat{A} \\
&\quad \times \left[\frac{1-(n^2-1)}{2n^2+1}\right]^2 \text{¡}\hat{A} \left[\frac{1-(D-1)}{2D+1}\right] \qquad (4)
\end{aligned}
$$

$$
\begin{aligned}
\beta_{xxx} &= \frac{1.5(6.6262 \times 10^{-34})^{-2}\,\mathrm{J^{-2}\,S^{-2}}\mu_{\mathrm{eg}}^2(\mu_{\mathrm{e}} - \mu_{\mathrm{g}})\lambda_{\mathrm{e}}^2}{c(1-\omega^2/\omega_{\mathrm{e}}^2)(1-4\omega^2/\omega_{\mathrm{e}}^2)} \\
&= \frac{3.8012(9^{-1} \times 10^{-9}\,\mathrm{C^2\,m^{-1}})^{-2}\mu_{\mathrm{eg}}^2(\mu_{\mathrm{e}} - \mu_{\mathrm{g}})\lambda_{\mathrm{e}}^2}{(1-\lambda_{\mathrm{e}}^2/\lambda_{\mathrm{a}}^2)(1-4\lambda_{\mathrm{e}}^2/\lambda_{\mathrm{a}}^2)} \qquad (5)
\end{aligned}
$$

It is all known that urea in solid state possesses a high second harmonic generation (SHG) value and could be used as double-frequency laser materials in the early days. We reported previously [25] for 10-methylacridone and 10-benzylacridone, the SHG values in powder was, respectively, 1.381 and 1.861 times of that value of urea, which was determined by Kurtz's method, therefore, in powder state, both compounds of 10-methylacridone and 10-benzylacridone possess a higher SHG value than urea does. For 10-methylacridone and 10-benzylacridone [25], the β_{xxx} values in DMSO was, respectively, (6.578 and 6.845) × $10^{-30}\,\mathrm{m^5\,C^{-1}}$ determined by solvatochromic method. It could be found from Table 4 that these thirteen trisubstituted-furan compounds, except **2db**, all showed a higher β_{xxx} value in DMSO, especially for **2dc** ($75.77 \times 10^{-30}\,\mathrm{m^5\,C^{-1}}$) and **2dd** ($83.32 \times 10^{-30}\,\mathrm{m^5\,C^{-1}}$), than that 10-methylacridone ($6.578 \times 10^{-30}\,\mathrm{m^5\,C^{-1}}$) or 10-benzylacridone ($6.845 \times 10^{-30}\,\mathrm{m^5\,C^{-1}}$) [25] in DMSO did.

According to the theory of organic nonlinear optical materials, the more the degree of intramolecular charge transfer, the higher the β_{xxx} value of this material, and the degree of intramolecular charge transfer depend on two factors: electronegativity-difference between electrowithdrawing group and electrodonating group and the length between electrowithdrawing group and electrodonating group. The difference of β_{xxx} value between acridone derivative and furan derivative could be suggested that as the electronegativity-difference between electrowithdrawing group and electrodonating group in acridone derivative molecule and in furan derivative molecule are nearly same, however, the length between electrowithdrawing group and electrodonating group in acridone derivative molecule are shorter than that in furan derivative molecule (Fig. 3), therefore, the degree of intramolecular charge transfer could be bigger in furan derivative molecule than that in acridone derivative molecule, consequently, the β_{xxx} values for furan derivative molecule should be bigger than that for acridone derivative molecule.

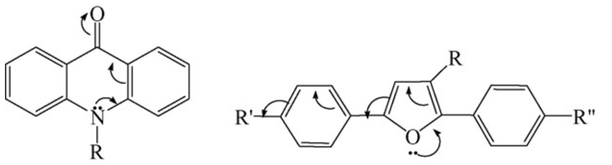

Fig. 3. The situation for intra molecular-charge-transfer for acridine derivative and furan.

In original, it was hoped that the β_{xxx} values for these furan derivative molecules, especially for **2ac**, **2bb**, **2bc**, **2ca**, **2cb**, **2da**, would be bigger than these β_{xxx} values which were obtained in this work. Because of the presence of substituent in 3-position of furan, the planes which two substituents in 2-, 5-position of furan were on and the furan ring plane were twisted out, which made the intramolecular-charge-transfer only occur between furan ring and one aromatic ring, the intramolecular-charge-tansfer length would become shorter, thus, the β_{xxx} values for these compounds synthesized in this work became less than that for the desired compound.

3. Experimental

3.1. Instruments and reagents

All melting point were determined on a 4× melting point microscope. ^{1}H, ^{13}C and ^{19}F NMR spectra were run on a Bruker AVANCE-300 NMR spectrometer. Ultraviolet spectra were recorded on a Shimadzu UV-1601 spectraphotometer. Fluorescence spectra were taken with a Shimadzu RF-5301PC spectro-fluorophotometer. Element analysis was taken with an Elementar Vario EL. Mass spectra were taken with a Shimadzu LCMS-2010A. *n*-Butyllithium (Alfa-Aesor), trifluoroaceticacid (Fluka), 4-fluorobenzaldehyde, 2,4-dimethoxybenzaldehyde, 4-hydroxybenzaldehyde, 4-trifluoromethylbenzaldehyde were of analytical grade and used without further purification. All the solvents were dried using standard methods before use.

3.2. The preparation of samples

Intermediate compounds **1a–d** and terminal compounds **2aa–2dd** were prepared, respectively, as Refs. [23,24].

3.2.1. Methyl 4-(2-(hex-1-ynyl)-1,3-dithiolan-2-yl)benzoate (*1a*) [24]

Yield: 67%, ^{1}H NMR (CdCl$_3$), δ, 0.91 (t, J = 7.5 Hz, 3H), 1.43 (tq, $J_1 = J_2$ = 7.4 Hz, 2H), 1.55 (tt, J_1 = 7.5 Hz, J_2 = 7.1 Hz, 2H), 2.34 (t, J = 7.1 Hz, 2H), 3.50 (m, 4H), 3.90 (s, 3H), 7.98 (s, 4H). ESI-MS for $C_{17}H_{21}O_2S_2$ ($M + \mathrm{H}^+$), 321.2.

3.2.2. 2-(2-Phenylethynyl)-2-(4-biphenyl)-1,3-dithiolane (*1b*)

Yield: 79%, mp 102–104 °C. ^{1}H NMR (CdCl$_3$), δ, 3.76 (m, 4H), 7.33 (m, 4H), 7.43 (m, 2H), 7.50 (m, 2H), 7.59 (m, 4H), 8.07

(d, $J = 10.5$ Hz, 2H). ^{13}C NMR (CdCl$_3$), δ, 43.0, 62.7, 87.4, 91.4, 122.9, 127.1, 127.2, 127.6, 128.2, 128.3, 128.4, 128.5, 128.9, 131.7, 137.8, 140.5, 141.3. ESI-MS for $C_{23}H_{19}S_2$ ($M + H^+$), 359.1.

3.2.3. 2-(2-Phenylethynyl)-2-(4-methoxyphenyl)-1,3-dithiolane (*1c*)

Yield: 78%, mp 92–94 °C. ^{1}H NMR (CdCl$_3$), δ, 3.75 (m, 4H), 3.82 (s, 3H), 6.90 (d, $J = 6.8$ Hz, 2H), 7.34 (m, 3H), 7.51 (m, 2H), 7.95 (d, $J = 6.6$ Hz, 2H). ^{13}C NMR (CdCl$_3$), δ, 41.8, 55.9, 62.6, 87.2, 91.9, 114.0, 123.3, 128.8, 128.9, 129.5, 130.7, 132.1, 160.1. ESI-MS for $C_{18}H_{17}OS_2$ ($M + H^+$), 313.0.

3.2.4. 2-(Naphthalen-3-yl)-2-(2-phenylethynyl)-1,3-dithiolane (*1d*)

Yield: 80%, mp 118–119 °C. ^{1}H NMR (CdCl$_3$), δ, 3.80 (m, 4H), 7.35 (m, 3H), 7.49 (m, 2H), 7.56 (m, 2H), 7.86 (m, 3H), 8.05 (d, $J = 10.0$ Hz, 3H), 8.47 (s, 1H). ^{13}C NMR (CdCl$_3$), δ, 41.7, 62.6, 87.2, 91.1, 122.7, 125.6, 126.3, 126.5, 127.4, 128.1, 128.2, 128.3, 128.4, 131.6, 132.6, 133.0, 136.0. ESI-MS for $C_{21}H_{16}S_2$ ($M + H^+$), 332.1.

3.2.5. Methyl 4-(4-butyl-5-(4-fluorophenyl)furan-2-yl)benzoate (*2aa*)

Yield: 45%, mp 82–83 °C. ^{1}H NMR (CdCl$_3$), δ, 0.98 (t, $J = 7.4$ Hz, 3H), 1.47 (tq, $J_1 = J_2 = 7.4$ Hz, 2H), 1.68 (tt, $J_1 = 7.4$ Hz, $J_2 = 8.0$ Hz, 2H), 2.69 (t, $J = 8.0$ Hz, 2H), 3.95 (s, 3H), 6.81 (s, 1H), 7.19 (t, $J = 8.7$ Hz, 2H), 7.68 (m, $J = 6.8$ Hz, 2H), 7.77 (d, $J = 8.5$ Hz, 2H), 8.07 (d, $J = 8.5$ Hz, 2H), ^{13}C NMR (CdCl$_3$), δ, 14.4, 23.0, 26.1, 32.5, 52.5, 111.8, 116.0, 116.3, 123.6, 124.4, 128.0, 128.7, 130.6, 135.1, 148.8, 151.2, 160.8, 164.0, 167.3. ^{19}F NMR (CdCl$_3$), δ, −114.45 (m). ESI-MS for $C_{22}H_{22}FO_3$ ($M + H^+$) 353.2. Anal. calcd. for $C_{22}H_{21}FO_3$: C, 74.98; H, 6.01. Found: C, 75.18; H, 6.12.

3.2.6. Methyl 4-(4-butyl-5-(4-trifluoromethylphenyl)furan-2-yl)benzoate (*2ab*)

Yield: 47%, mp 99–100 °C. ^{1}H NMR (CdCl$_3$), δ, 1.00 (t, $J = 7.2$ Hz, 3H), 1.50 (tq, $J_1 = J_2 = 7.3$ Hz, 2H), 1.72 (tt, $J_1 = 7.2$ Hz, $J_2 = 8.0$ Hz, 2H), 2.76 (t, $J = 8.0$ Hz, 2H), 3.96 (s, 3H), 6.83 (s, 1H), 7.71 (d, $J = 8.5$ Hz, 2H), 7.79 (d, $J = 8.3$ Hz, 2H), 7.83 (d, $J = 8.5$ Hz, 2H), 8.09 (d, $J = 8.3$ Hz, 2H). ^{13}C NMR (CdCl$_3$), δ, 14.4, 23.0, 26.3, 32.4, 52.6, 67.6, 112.0, 123.9, 125.9, 126.0, 128.9, 130.6, 134.7, 135.0, 148.0, 152.1, 167.2. ^{19}F NMR (CdCl$_3$), δ, −62.94 (s). ESI-MS for $C_{23}H_{22}F_3O_3$ ($M + H^+$) 403.0. Anal. calcd. for $C_{23}H_{21}F_3O_3$, C, 68.65; H, 5.26. Found: C, 68.35; H, 5.51.

3.2.7. Methyl 4-(4-butyl-5-(2,4-dimethoxylhenyl)furan-2-yl)benzoate (*2ac*)

Yield: 53%, viscose liquid. ^{1}H NMR (CdCl$_3$), δ, 0.92 (t, $J = 7.4$ Hz, 3H), 1.37 (tq, $J_1 = 7.4$ Hz, $J_2 = 7.6$ Hz, 2H), 1.59 (tt, $J_1 = 7.6$ Hz, $J_2 = 8.1$ Hz, 2H), 2.45 (t, $J = 8.0$ Hz, 2H), 3.85 (s, 3H), 3.88 (s, 3H), 3.93 (s, 3H), 6.60 (m, $J = 8.3$ Hz, 2H), 6.83 (s, 1H), 7.39 (t, $J = 8.3$ Hz, 2H), 7.74 (m, $J = 8.5$ Hz, 2H), 8.05 (d, $J = 8.6$ Hz, 2H). ^{13}C NMR (CdCl$_3$), δ, 14.4, 23.0, 25.7, 32.7, 52.5, 55.9, 99.3, 105.1, 110.8, 113.7, 123.5, 125.5, 128.2, 130.5, 132.1, 135.7, 148.0, 151.6, 158.7, 161.7, 167.4.

3.2.8. 2-(2,4-dimethoxyphenyl)-3-phenyl-5-(4-biphenyl)furan (*2ba*)

Yield: 35%, mp 50–52 °C. ^{1}H NMR (CdCl$_3$), δ, 3.52 (s, 3H), 3.90 (s, 3H), 6.55 (s, 1H), 6.65 (d, $J = 8.6$ Hz, 1H), 7.06 (s, 1H), 7.44 (m, 10H), 7.71 (d, $J = 8.1$ Hz, 4H), 7.88 (d, $J = 8.3$ Hz, 2H). ^{13}C NMR (CdCl$_3$), δ, 55.8, 56.1, 99.7, 105.3, 108.2, 114.3, 124.4, 124.8, 125.4, 127.5, 127.8, 127.9, 128.0, 128.1, 128.7, 129.3, 129.4, 130.5, 132.4, 135.4, 140.4, 141.3, 146.8, 153.2, 153.5, 158.8, 162.1, 162.2. ESI-MS for $C_{30}H_{25}O_3$ ($M + H^+$), 433.2.

3.2.9. 2-(4-fluorophenyl)-3-phenyl-5-(4-biphenyl)furan (*2bb*)

Yield: 38%, mp 176–178 °C. ^{1}H NMR (CdCl$_3$), δ, 6.88 (s, 1H), 7.06 (t, $J = 8.7$ Hz, 2H), 7.42 (m, 4H), 7.49 (m, 4H), 7.66 (m, 6H), 8.25 (d, $J = 8.6$ Hz, 2H). ^{13}C NMR (CdCl$_3$), δ, 110.0, 115.8, 116.1, 124.6, 127.4, 127.9, 128.4, 128.5, 129.1, 129.3, 129.8, 134.5, 140.7, 141.0, 147.6, 152.8. ^{19}F NMR (CdCl$_3$), δ, −113.99 (m). ESI-MS for $C_{28}H_{20}FO$ ($M + H^+$) 391.2.

3.2.10. 2-(4-Cyanophenyl)-3-phenyl-5-(4-biphenyl)furan (*2bc*)

Yield: 26%. ^{1}H NMR (CdCl$_3$), δ, 6.88 (s, 1H), 7.50 (m, 10H), 7.42 (d, $J = 8.5$ Hz, 2H), 7.69 (m, 8H), 7.85 (m, 2H). ^{13}C NMR (CdCl$_3$), δ, 110.7, 110.9, 119.6, 125.1, 126.3, 127.5, 127.8, 128.1, 128.5, 129.0, 129.4, 132.9, 134.2, 135.6, 141.0, 141.5, 146.3, 154.3.

3.2.11. 2-(4-Cyanophenyl)-5-(4-methoxyphenyl)-3-phenylfuran (*2ca*)

Yield: 24%, mp 137–139 °C. ^{1}H NMR (CdCl$_3$), δ, 3.89 (s, 3H), 6.71 (s, 3H), 7.00 (d, $J = 8.8$ Hz, 2H), 7.46 (m, 6H), 7.56 (d, $J = 8.6$ Hz, 2H), 7.68 (d, $J = 8.7$ Hz, 2H), 7.73 (d, $J = 8.9$ Hz, 2H). ^{13}C NMR (CdCl$_3$), δ, 55.8, 109.2, 110.2, 114.8, 115.9, 119.5, 122.9, 123.3, 125.9, 128.4, 129.1, 129.4, 130.3, 132.7, 134.2, 135.6, 145.4, 154.5, 160.2. ESI-MS for $C_{24}H_{18}NO_2$ ($M + H^+$) 352.2.

3.2.12. 2-(4-Fluorophenyl)-5-(4-methoxyphenyl)-3-phenylfuran (*2cb*)

Yield: 67%, mp 90–92 °C. ^{1}H NMR (CdCl$_3$), δ, 3.88 (s, 3H), 6.70 (s, 1H), 7.00 (m, 4H), 7.45 (m, 5H), 7.58 (dd, $J_1 = 8.9$ Hz, $J_2 = 5.4$ Hz, 2H), 7.71 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR (CdCl$_3$), δ, 55.8, 108.3, 114.8, 115.7, 116.0, 122.9, 123.9, 124.6, 125.7, 127.8, 128.0, 128.2, 128.3, 129.1, 129.2, 134.7, 146.8, 153.1, 159.7. ^{19}F NMR (CdCl$_3$), δ, −114.464 (m). ESI-MS for $C_{23}H_{18}FO_2$ ($M + H^+$) 345.1. Anal. calcd for $C_{23}H_{17}FO_2$: C, 80.22; H, 4.98. Found: C, 80.01; H, 5.12.

3.2.13. 2-(4-Hydroxyphenyl)-5-(4-methoxyphenyl)-3-phenylfuran (*2cc*)

Yield: 51%, mp 170–173 °C. ^{1}H NMR (CdCl$_3$), δ, 6.73 (s, 1H), 6.88 (d, $J = 8.8$ Hz, 2H), 7.01 (d, $J = 8.9$ Hz, 2H), 7.41 (m, 3H), 7.52 (m, 3H), 7.74 (d, $J = 8.9$ Hz, 2H). ^{13}C NMR (CdCl$_3$),

δ, 55.8, 108.3, 114.6, 115.8, 125.6, 127.5, 128.2, 129.0, 134.7, 146.8, 153.1, 159.7. ESI-MS for $C_{23}H_{19}O_3$ ($M+H^+$), 343.1.

*3.2.14. 2-(4-Fluorophenyl)-5-(naphthalen-2-yl)-3-phenylfuran (**2da**)*

Yield: 33%, mp 130–132 °C. ^{1}H NMR ($CdCl_3$), δ, 6.96 (s, 1H), 7.06 (t, $J=8.8$ Hz, 2H), 7.46 (m, 7H), 7.77 (m, 2H), 8.07 (m, 4H), 8.25 (s, 1H). ^{13}C NMR ($CdCl_3$), δ, 110.5, 115.8, 116.1, 122.6, 124.8, 126.5, 127.0, 127.8, 127.9, 128.2, 128.3, 128.5, 128.6, 128.9, 129.1, 129.2, 133.3, 134.0, 134.5, 147.8, 153.1, 161.0, 164.3. ESI-MS for $C_{26}H_{18}FO$ ($M+H^+$), 364.9.

*3.2.15. 2-(2,4-Dimethoxyphenyl)-5-(naphthalen-2-yl)-3-phenylfuran (**2db**)*

Yield: 28%, mp 47–49 °C. ^{1}H NMR ($CdCl_3$), δ, 3.50 (s, 3H), 3.90 (s, 3H), 6.52 (s, 1H), 6.62 (d, $J=8.6$ Hz, 1H), 7.10 (s, 1H), 7.32 (m, 6H), 7.40 (m, 3H), 7.87 (m, 4H), 8.23 (s, 1H). ^{13}C NMR ($CdCl_3$), δ, 55.6, 55.9, 99.5, 105.3, 108.4, 114.1, 122.4, 122.8, 125.3, 126.2, 126.8, 127.6, 128.2, 128.6, 128.7, 128.8, 132.3, 133.1, 134.1, 135.2, 146.8, 153.3, 158.7, 162.0. ESI-MS for $C_{28}H_{23}O_3$ ($M+H^+$), 407.2.

*3.2.16. 2-(4-Hydroxyphenyl)-5-(naphthalen-2-yl)-3-phenylfuran (**2dc**)*

Yield: 40%, mp 141–143 °C. ^{1}H NMR ($CdCl_3$), δ, 6.84 (d, $J=8.8$ Hz, 2H), 6.95 (s, 1H), 7.41 (m, 3H), 7.53 (m, 6H), 7.86 (m, 4H), 8.25 (s, 1H). ^{13}C NMR ($CdCl_3$), δ, 110.3, 115.9, 122.4, 122.7, 123.7, 124.6, 126.3, 127.0, 127.6, 128.3, 128.4, 128.5, 128.6, 128.9, 129.1, 133.1, 134.1, 134.8, 152.8, 155.6. ESI-MS for $C_{26}H_{19}O_2$ ($M+H^+$), 363.2.

*3.2.17. 4-(5-(naphthalen-2-yl)-3-phenylfuran-2-yl)phenyl acrylate (**2dd**)*

Yield: 69%, mp 121–123 °C. ^{1}H NMR ($CdCl_3$), δ, 6.09 (d, $J=10.4$ Hz, 1H), 6.40 (dd, $J_1=10.4$ Hz, $J_2=10.6$ Hz, 1H), 6.66 (d, $J=10.7$ Hz, 1H), 6.99 (s, 1H), 7.18 (d, $J=8.6$ Hz, 2H), 7.47 (m, 7H), 7.74 (d, $J=8.7$ Hz, 2H), 7.91 (m, 4H), 8.29 (s, 1H). ^{13}C NMR ($CdCl_3$), δ, 110.6, 122.1, 122.6, 125.3, 126.5, 127.0, 127.7, 127.9, 128.2, 128.3, 128.7, 128.9, 129.2, 129.3, 133.2, 133.3, 134.0, 147.9, 150.3, 153.2, 164.9. ESI-MS for $C_{29}H_{21}O_3$ ($M+H^+$), 417.2. Anal. calcd. for $C_{29}H_{20}O_3$: C, 83.63; H, 4.84. Found: C, 83.33; H, 5.01.

Acknowledgements

This project is supported by Scientific and Technical Project foundation of Guangdong Province (2003C103006) and HCS thanks Professor T.-Y. Luh (Taiwan University, Taiwan) for his help on author's research work.

References

[1] M. Ahlheim, M. Barzoukas, V.P. Bedworth, M. Blanchard-Desce, A. Fort, Z.-Y. Hu, R.S. Marder, W.J. Perry, C. Runser, M. Staehelin, B. Zysset, Science 271 (1996) 355.
[2] J.-D. Luo, J.-L. Hua, J.-G. Qin, J.-Q. Cheng, Y.-C. Shen, Z.-H. Lu, P. Wang, C. Ye., Chem. Commun. (2001) 171.
[3] (a) I.V. Ion, S. Charier, L. Moreaux, J. Mertz, M. Blanchard-Desce, Angew. Chem. Int. Ed. 40 (2001) 2098;
(b) O. Mongin, L. Porres, L. Moreaux, J. Mertz, M. Blanchard-Desce, Org. Lett. 4 (2002) 719.
[4] (a) Z.L. Huang, N. Li, H. Lei, Z.R. Qin, H.Z. Wang, Z.P. Zhong, Z.H. Zhou, Chem. Commun. (2002) 2400;
(b) Z.L. Huang, N. Li, Y.-F. Sun, H.-Z. Wang, H.-C. Song, Z.-L. Xu, J. Mol. Struct. 657 (2003) 343.
[5] G.S. He, P.P. Markowlcz, T.-C. Lin, P.N. Prasad, Nature 415 (2002) 767.
[6] S. Kawata, H.B. Sun, T. Tanaka, K. Takada, Nature 412 (2001) 697.
[7] K.-T. Wang, Y.-Y. Chien, R.-T. Chen, C.-F. Wang, Y.-T. Lin, H.-H. Chiang, P.-Y. Hsieh, C.-C. Wu, C.H. Chou, Y.O. Su, G.-H. Lee, S.-M. Peng, J. Am. Chem. Soc. 124 (2002) 11576.
[8] (a) C.W. Kao, Y.T. Tao, Appl. Phys. Lett. 79 (2001) 4234;
(b) Y. Liu, J. Gao, H. Zhang, Y. Wang, Angew. Chem. Int. Ed. 41 (2002) 182;
(c) L.-Z. Zhang, C.W. Chen, C.-F. Lee, C.C. Wu, T.Y. Luh, Chem. Commun. (2002) 2336.
[9] M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, Nature 395 (1998) 151.
[10] C.C. Wu, C.-W. Chen, Y.-T. Lin, H.-L. Yu, J.-H. Hsu, T.-Y. Luh, Appl. Phys. Lett. 79 (2001) 3023.
[11] (a) J.M. Tour, Acc. Chem. Res. 33 (2000) 791;
(b) U. Mitschke, E.M. Osteritz, T. Debaerdernaeker, M. Sokolowski, P. Bäuerle, Chem. Eur. J. 4 (1998) 2211.
[12] T.K.R. Justin, J.T. Lin, Y.-T. Tao, C.-W. Ko, Chem. Mater. 14 (3) (2002) 1354.
[13] J. Liu, Q.-Q. Zhou, Y.-X. Cheng, Y.-H. Geng, L.-X. Wang, D.-G. Ma, X.-B. Jing, F.-S. Wang, Adv. Mater. 17 (24) (2005) 2974.
[14] A. Facchetti, J. Letizia, M.-H. Yoon, M. Mushrush, H.E. Katz, T.J. Marks, Chem. Mater. 16 (23) (2004) 4715.
[15] Y.-G. Hisao, Y. Atsutoshi, H. Shu, K. Shunsuke, J. Appl. Phys. 96 (8) (2004) 4240.
[16] I. Musubu, H. Ryota, I. Masamitsu, H. Takeshi, H. Shu, K. Toshiki, T. Yoshio, Adv. Mater. 15 (3) (2003) 213.
[17] H. Ryota, N. Michifumi, H. Shu, I. Musubu, K. Toshiki, T. Yoshio, Adv. Mater. 14 (2) (2002) 119.
[18] M. Melissa, F. Antonio, L. Michael, K.E. Howard, M.J. Tobin, J. Am. Chem. Soc. 125 (31) (2003) 9414.
[19] K.E. Howard, H.X. Michael, D. Ananth, S. Rahul, J. Appl. Phys. 91 (3) (2002) 1572.
[20] K. Masui, A. Mori, K. Okano, K. Takamura, Org. Lett. 6 (12) (2004) 2011.
[21] Y.-J. Cheng, S. Basu, S.-J. Luo, T.-Y. Luh, Macromolecules 38 (4) (2005) 1442.
[22] C.-C. Wu, W.-Y. Hung, T.-L. Liu, L.-Z. Zhang, T.-Y. Luh, J. Appl. Phys. 93 (9) (2003) 5465.
[23] C.-F. Lee, C.-Y. Liu, H.-C. Song, T.-Y. Luh, Chem. Commun. (2002) 2824.
[24] C.-F. Lee, L.-M. Yang, T.-Y. Hwu, A.-S. Feng, J.-C. Tseng, T.-Y. Luh, J. Am. Chem. Soc. 122 (2000) 4992.
[25] H.-C. Song, Y.-W. Chen, X.-L. Zheng, B.-N. Ying, Spectrochim. Acta A 57 (2001) 1717.
[26] H.-C. Song, R.-J. Jin, X.-L. Zheng, B.-N. Ying, Spectrochim. Acta A 57 (2001) 2729.
[27] H.-C. Song, W.-M. Li, G.-R. Liu, Z.-L. Xu, Spectrochim. Acta A 59 (2003) 2041.
[28] H.-C. Song, H. Wen, W.-M. Li, Spectrochim. Acta A 60 (2004) 1587.
[29] J. Guilford II., J.R. Willliam, C. Chol-Yoo, J. Phys. Chem. 89 (1985) 294.
[30] H. Inomata, K. Goushi, T. Masuko, T. Konno, T. Imai, H. Sasabe, J.J. Brown, C. Adachi, Chem. Mater. 16 (2004) 1285.