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Synthesis and Properties of Alkyl Chain Substituted Naphthalenetetracarboxylic Monoanhydride Monoimides and Unsymmetrically Substituted Naphthalene Derivatives

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1,4,5,8-Naphthalenedianhydride is converted to *N*-(2-ethylhexyl)-1,4,5,8-naphthalenetetracarboxylic monoanhydride monoimide (**2a**) and *N*-(2-hydroxyethyl)-1,4,5,8-naphthalenetetracarboxylic monoanhydride monoimide (**2c**) through the potassium salt prepared from a reaction with potassium hydroxide. *N*-Dodecyl-1,4,5,8-naphthalenetetracarboxylic monoanhydride monoimide (**2b**) was prepared by the condensation reaction of 1,4,5,8-naphthalenedianhydride with dodecylamine. Naphthalene-1,4-*N*-(2-ethylhexyl)-imide-*N*-ethyl-1*H*-benzo[d]imidazol-5-carboxylate and naphthalene-1,4-*N*-dodecyl-imide-*N*-ethyl-1*H*-benzo[d]imidazol-5-carboxylate were prepared by the condensation reaction of *N*-alkyl-1,4,5,8-naphthalenetetracarboxylic monoanhydride monoimide (alkyl = 2-ethylhexyl and dodecyl) with ethyl 3,4-diaminobenzoate. Molecular structures and electrochemical properties of all naphthalene derivatives were determined. Their thermal properties were also studied by thermal gravimetric analysis.

Keywords: Condensation reaction, Monopotassium salt, Monoanhydride monoimides.

INTRODUCTION

Since the photovoltaics are clean energy sources and reduces the dependency on fossil fuels, public and private sectors' interest on this technology are highly appreciated [1,2]. Using of thin films of organic dyes with conjugated π-electron system increases in recent years like organic light-emitting diodes (OLED) and solar cells [3-11]. Due to their high thermal and chemical stabilities and excellent photoconductive properties, the organic pigments or dyes are attracted much attention [12-15].

Previously prepared 1,4,5,8-naphthalenedianhydride was converted to *N*-(2-ethylhexyl)-1,4,5,8-naphthalenetetracarboxylic monoanhydride monoimide (**2a**) and *N*-(2-hydroxyethyl)-1,4,5,8-naphthalenetetracarboxylic monoanhydride monoimide (**2c**) through the condensation reaction in the presence of potassium salt (Path A) (**Scheme-I**) by the application of previously published procedure [16]. *N*-dodecyl-1,4,5,8-naphthalenetetracarboxylic monoanhydride monoimide (**2b**) was obtained by another procedure in which it was the condensation of 1,4,5,8-naphthalenedianhydride with dodecylamine (Path B) (**Scheme-I**) [17]. Unsymmetrically naphthalene derivatives (**3a-b**) were obtained by the condensation of the *N*-alkyl-1,4,5,8-naphthalenetetracarboxylic monoanhydride monoimide (**2a-b**) with ethyl 3,4-diaminobenzoate.

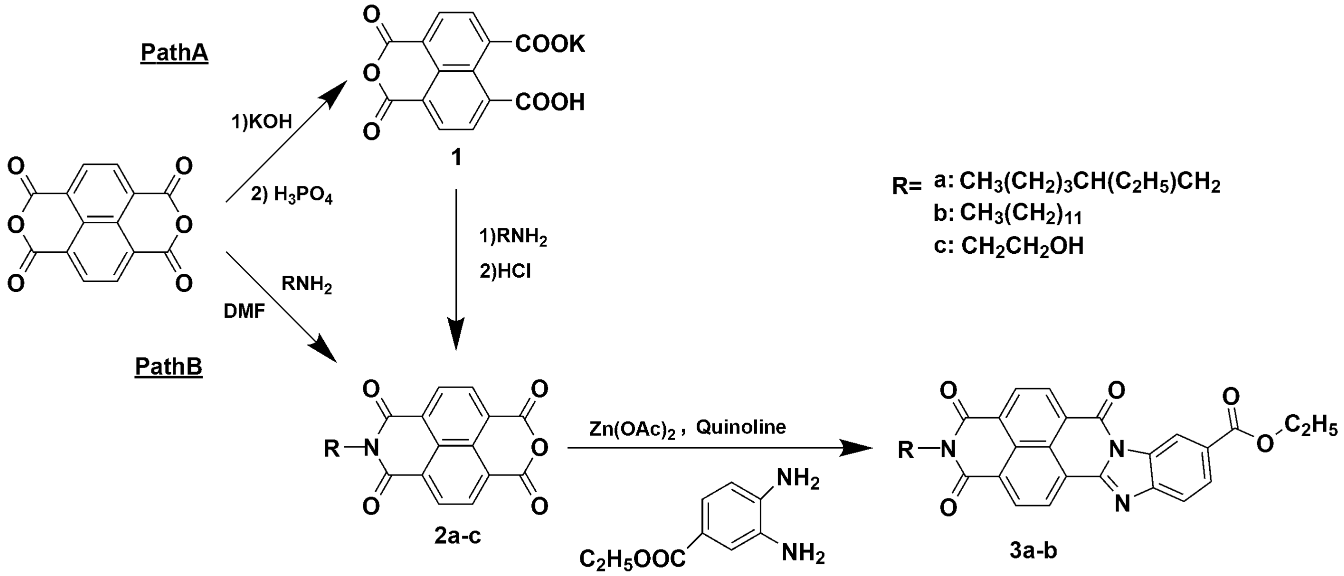
In this present paper, the synthesis of monoimides and unsymmetrically naphthalene derivatives having an alkyl chain are described (**Scheme-I**). The thermal stabilities and electrochemical properties of these derivatives are also reported.

EXPERIMENTAL

1,4,5,8-Naphthalenedianhydride, 2-ethylhexylamine, 2-aminoethanol, zinc acetate, quinoline, sodium carbonate, hydrochloric acid (36-38 %), *ortho*-phosphoric acid, potassium hydroxide, acetic acid (glacial), potassium carbonate, sodium perchlorate, ammonium solution (25%) were obtained Fluka and Merck and used as supplied. All organic solvents (chloroform, ethanol, acetonitrile, dimethyl formamide, dimethyl sulfoxide) were of spectrophotometric grade.

Synthesis of naphthalene-1,4,5,8-tetracarboxylic acide monoanhydride monopotassium carboxylate (1) [16]: 1,4,5,8-Naphthalenedianhydride (7.6 mmol), 35 mL ratio of 5 % potassium hydroxide were under stirring heated to 90 °C. 12.5 mL ratio of 10 % *ortho*-phosphoric acid was then added dropwise to the reaction mixture. After further stirring at 90 °C, the precipate was filtered, washed thourougly with water and dried overnight in vacuum dessicator.

Synthesis of N-(2-ethylhexyl)-1,4,5,8-naphthalenetetracarboxylic monoanhydride monoimide (2a) [16]: Naphtha-



Scheme-I: Synthetic routes of N-alkyl-1,4,5,8-naphthalenetetracarboxylic monoanhydride monoimides (**2a-c**) and unsymmetrical naphthalene derivatives (**3a-b**)

lene-1,4,5,8-tetracarboxylic acide monoanhydride monopotassium carboxylate (2.2 mmol), 2-ethylhexylamine (11 mmol) and 40 mL of water was stirred at 0-5 °C for 3 h, heated at 90 °C for 1 h with stirring and then 12.5 mL ratio of 25 % aqueous solution of potassium carbonate was added. Reaction mixture was acidified by the addition of 5 % hydrochloric acid solution and the resulting precipate was filtered, washed with water to remove residual amine, dried overnight in vacuum dessicator. Molecular structure was monitored by means of FT-IR, ^{1}H NMR, ^{13}C NMR. FT-IR (KBr, ν_{max}, cm^{-1}): 1791, 1763, 1708 (C=O), 1669 (imide), 1080 (C-O); ^{1}H NMR (400 MHz, $CDCl_3$): 8.72 (s, 4H), 4.12 (t, 2H), 1.93 (m, 1H), 1.34 (m, 8H), 0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.80, 159.05, 133.35, 131.47, 129.09, 128.13, 127.11, 123.02, 45.05, 38.16, 30.91, 28.80, 24.25, 23.22, 14.24, 10.78.

Synthesis of *N*-dodecyl-1,4,5,8-naphthalenetetracarboxylic monoanhydride monoimide (2b) [17]: 1,4,5,8-Naphthalenedianhydride (7.46 mmol) was dissolved in 20 mL of dry DMF and heated to reflux under argon. Dodecylamine (4 mmol) diluted in 10 mL of dry DMF was then added dropwise to the refluxing solution over the period of 1 h. After refluxing the whole solution for 8 h, the mixture was added into cold diethylether. The precipate was filtered, washed with diethylether, then chloroform and dried overnight in vacuum dessicator. Molecular structure was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR. FT-IR (KBr, ν_{max}, cm^{-1}): 1789, 1770, 1709 (C=O), 1659, 1080 (imide). ^{1}H NMR (400 MHz, ppm in $CDCl_3$): 8.74 (s, 4H), 4.19 (t, 2H), 1.72 (m, 2H), 1.36 (m, 18H), 0.87 (m, 3H); ^{13}C NMR (100 MHz, ppm in $CDCl_3$): 162.41 (C=O) , 159.04 (C=O) 133.34, 131.41, 128.17, 123.04, 41.44, 32.12, 29.82, 29.78, 29.72, 29.54, 29.50, 28.24, 27.27, 22.88, 14.30.

Synthesis of N-(2-Hydroxyethyl)-1,4,5,8-naphthalenetetracarboxylic monoanhydride monoimide (2c) [16]: Naphthalene-1,4,5,8-tetracarboxylic acid monoanhydride monopotassium carboxylate (2.2 mmol), 2-aminoethanol (11 mmol) and 40 mL of water was stirred at 0-5 °C for 3 h, heated at 90 °C for 2 h with stirring and then 12.5 mL ratio of 25 % aqueous solution of potassium carbonate was added. Reaction mixture was acidified by the addition of 5 % hydrochloric acid solution and the resulting precipate was filtered, washed with water to remove residual amine and finally dried overnight in vacuum dessicator. Molecular structure was identified by means of ^{1}H NMR, ^{13}C NMR. ^{1}H NMR spectra (400 MHz, ppm in DMSO): 8.52 (d, 2H), 8.17 (d, 2H), 4.14 (t, 2H), 3.62 (t, 2H), 2.45 (s, OH); ^{13}C NMR (100 MHz, ppm in DMSO): 169.19 (C=O), 163.66 (C=O), 137.48, 130.71, 129.87, 129.30, 126.17, 125.36, 58.44, 42.85.

Synthesis of ethyl 3,4-diaminobenzoate [18]: Dry H_2SO_4 (3 mL) treated over dry ethanol (30 mL) until the weight increased 10 % and 3,4-diaminobenzoic acid (1 g) was added into this acid mixture and the mixture was heated under reflux with stirring for 20 h [19]. To this mixture deionized water (30 mL) was added, and then the dark brown solution was neutralized by Na_2CO_3. The precipate was filtered, recrystallized from water and dried under vacuum overnight. Molecular structure was analyzed by means of FT-IR, ^{1}H NMR, ^{13}C NMR. FT-IR (KBr, ν_{max}, cm^{-1}): 1735 (C=O), ^{1}H NMR (400 MHz, ppm in $CDCl_3$): 7.46 (m, 2H), 6.67 (d, 1H), 4.30 (m, 2H), 3.54 (broad s, 4H), 1.35 (t, 3H); ^{13}C NMR (100 MHz, ppm in $CDCl_3$): 167.09 (C=O), 140.53 (C–NH_2),133.32 (C–NH_2), 123.47, 121.78, 118.59, 115.14, 60.57, 14.62.

Synthesis of naphthalene-1,4-*N*-(2-ethylhexyl)-imide-*N*-ethyl-1*H*-benzo[d]imidazol-5-carboxylate (3a): *N*-(2-Ethylhexyl)-1,4,5,8-naftalenetetracarboxylic monoanhydride monoimide (0.181 mmol), ethyl 3,4-diaminobenzoate (0.362 mmol), zinc acetate (0.0543 mmol) was dissolved in 25 mL of quinoline. The temperature was gradually increased to 200 °C. The mixture was kept at this temperature for 7 h under nitrogen atmosphere. The warm solution poured slowly into 2 molar ratio of 30 mL HCl. The precipate was filtered and washed thoroughly 10 % Na_2CO_3. Product dried under vacuum over a night at 100 °C. Molecular structure was characterized by means of ^{1}H NMR. ^{1}H NMR (400 MHz, ppm in $CDCl_3$): 9.1

(s, 1H), 8.9 (m, 1H), 8.8 (m, 1H), 8.5 (s, 1H), 8.5 (d, 1H), 8.2 (d, 1H), 7.9 (d, 1H), 4.5 (m, 2H), 4.1 (m, 2H), 1.9 (m, 1H), 1.4 (m, 9H), 0.9 (m, 6H).

Synthesis of naphthalene-1,4-*N*-dodecyl-imide-*N*-ethyl-1*H*-benzo[d]imidazol-5-carboxylate (3b): *N*-Dodecyl-1,4,5,8-naphthalenetetracarboxylic monoanhydride monoimide (0.181 mmol), ethyl 3,4-diaminobenzoate (0.362 mmol), zinc acetate (0.0543 mmol) was dissolved in 25 mL of quinoline. The temperature was gradually increased to 200 °C. The mixture was kept at this temperature for 7 h under nitrogen. The warm solution poured slowly into 2 molar ratio of 30 mL HCl. The precipate was filtered and washed thoroughly by 10% Na_2CO_3. The product was dried under vacuum overnight at 100 °C. Molecular structure was characterized by means of ^{1}H NMR. ^{1}H NMR (400 MHz, ppm in $CDCl_3$): 8.74 (s, 4H), 4.19 (t, 2H), 1.72 (m, 2H), 1.36 (m, 18H), 0.87 (m, 3H); ^{13}C NMR (100 MHz, ppm in $CDCl_3$): 162.41 (C=O) , 159.04 (C=O) 133.34, 131.41, 128.17, 123.04, 41.44, 32.12, 29.82, 29.78, 29.72, 29.54, 29.50, 28.24, 27.27, 22.88, 14.30.

Cyclic voltammetry measurements: Cyclic voltammetry (CV) measurements were carried out in DMSO by using a 3-electrode cell with a polished 2 mm glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode; the solution was 10^{-3} M in electroactive material and 0.2 M supporting electrolyte, sodium perchlorate; the instrument was Metrohm 746 VA Trace Analyser; ferrocene was the internal reference electrode $NaClO_4$ dissolved in DMSO under nitrogen gas protection at a scan rate of 100 mV/s at 25 °C. All solutions were purged with nitrogen for at least 10 min before starting the measurements.

RESULTS AND DISCUSSION

Electrochemistry of synthesized naphthalene derivatives: Cyclic voltammetry is a valuable tool to study reversible redox behaviour, electrochemical stability and to get information about LUMO energy values of the material under investigation. Measured potentials and the calculated LUMO values are summarized in Table-1. The LUMO energy values were calculated based on the value of 4.8 eV for ferrocene (Fc) with respect to zero vacuum level [20,21]. All of synthesized naphthalene derivatives exhibited two cathodic peaks and two anodic peaks in solution. For example, the cyclic voltammogram (Fig. 1) of naphthalene-1,4-*N*-(2-ethylhexyl)-imide-*N*-ethyl-1*H*-benzo[d]imidazol-5-carboxylate displays two cathodic peaks (at -0.44 and -0.80 V) and two anodic peaks (at -0.36 V and -0.73 V) and two reversible steps of reductions (at -0.40 V and -0.77 V) with respect to Ag/AgCl in DMSO corresponding to the first and second electron processes . The reduction potential with respect to ferrocene is -0.87 and -1.24 V and the corresponding LUMO energy leves is calculated as -3.93 eV. These results are comparable with those obtained by Uzun *et al.* [22] for 1,4,5,8-naphthalenediimide derivatives in chloroform solution and the reported LUMO value was -3.91 eV.

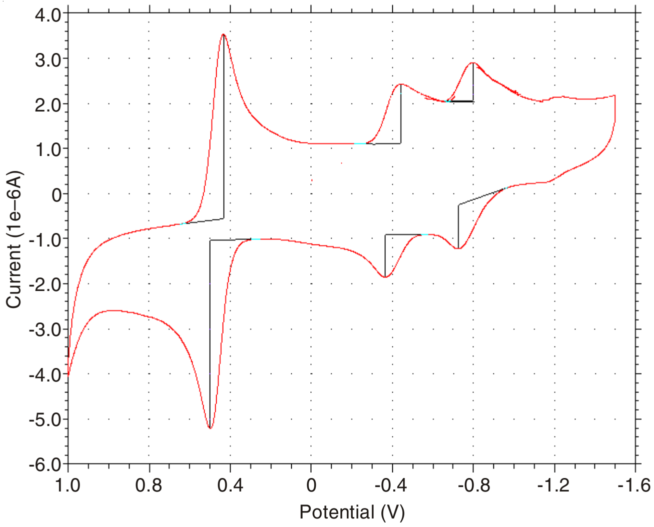


Fig. 1. Cyclic voltammogram of naphthalene-1,4-N-(2-ethylhexyl)-imide-N-ethyl-1*H*-benzo[d]imidazol-5-carboxylate (**3a**) (in DMSO, supporting electrolyte 0.2 M sodium perchlorate, scan rate 100 mV s^{-1}) at 25 °C

Thermal stability of synthesized naphthalene derivatives: Naphthalene diimides have long been known to be thermal and photostable compounds [23]. Thermal stability of synthesized naphthalene derivatives was determined by means of thermal gravimetric (TGA) measurements. Their TGA thermograms are shown in Figs. 2 and 3. All TGA curves show multistep weight loss. The highest and the lowest decomposition temperature were shown by **3b** and **2c**, respectively. The initial weight loss of 5.5 % (up to 225 °C) for **2c** corresponds to the degradation of hydroxyl group and 72 % (up to 510 °C) for **2b** corresponds to the degradation of alkyl group attached

TABLE-1
CYCLIC VOLTAMMETRY DATA AND LUMO ENERGY VALUE OF N-ALKYL-1,4,5,8-NAPHTHALENETETRACARBOXYLIC MONOANHYDRIDE MONOIMIDE [ALKYL = ETHYLHEXYL (**2a**), DODECYL (**2b**), ETHANOL (**2c**)] AND UNSYMMETRICAL NAPHTHALENE DERIVATIVES [(**3a**), (**3b**)] IN DMSO. [$E_{1/2}$/(V) *vs.* Fc = ($E_{1/2}$/V *vs.* Ag/AgCl) – (E_{Fc}/V *vs.* Ag/AgCl)]

Compounds	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$ (V) *vs.* Ag/AgCl	E_{Fc} (V) *vs.* Ag/AgCl	$E_{1/2}$ (V) *vs.* Fc	LUMO (eV)
2a	-0.40	-0.34	-0.37	0.468	-0.83	-3.96
	-0.80	-0.74	-0.77	0.468	-1.23	
2b	-0.41	-0.34	-0.37	0.468	-0.83	-3.45
	-0.79	-0.73	-0.76	0.468	-1.22	
2c	-0.40	-0.34	-0.37	0.476	-0.84	-3.95
	-0.91	-0.70	-0.81	0.476	-1.28	
3a	-0.44	-0.36	-0.40	0.466	-0.87	-3.93
	-0.80	-0.73	-0.77	0.466	-1.24	
3b	-0.44	-0.34	-0.39	0.476	-0.87	-3.93
	-0.78	-0.71	-0.74	0.476	-1.22	

(Supporting electrolyte, 0.2 M sodium perchlorate, Scan rate 100 mV s^{-1}, [**2a**] = [**2b**] = [**2c**] = [**3a**] = [**3b**] = 1 × 10^{-3} M).

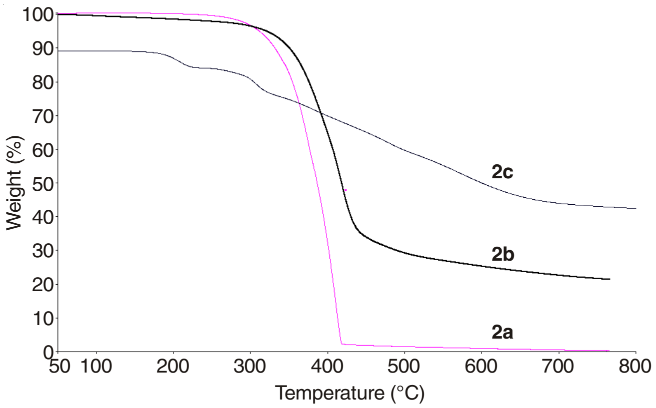


Fig. 2. Thermogravimetric analysis curves of **2a**, **2b**, **2c** at a heating rate 10 °C min^{-1} in N_2 atmosphere

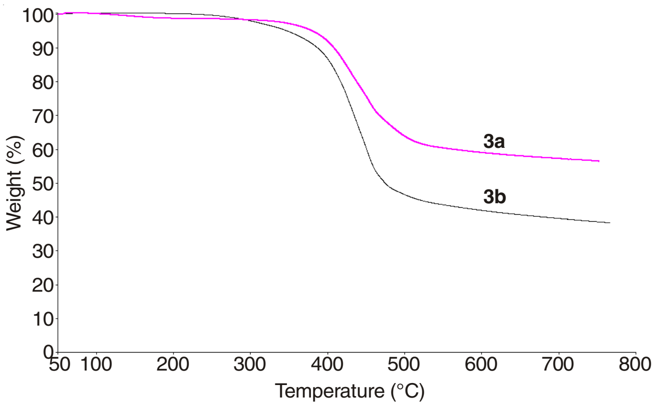


Fig. 3. Thermogravimetric analysis curves of **3a**, **3b** at a heating rate 10 °C min^{-1} in N_2 atmosphere

through imide linkage and partial degradation of anhydride 41 % weight loss (up to 550 °C) for **3b** corresponds to the degradation of alkyl group of imide in the molecule. Decomposition temperature of naphthalene-1,4-*N*-dodecyl-imide-*N*-ethyl-1*H*-benzo[d]imidazol-5-carboxylate starts from 310 °C and finished at 700 °C.

Conclusion

A novel unsymmetrical naphthalene derivatives were synthesized from N-alkyl-1,4,5,8-naphthalene tetracarboxylic monoanhydride monoimide. Since the naphthalene derivatives have different possibilities in terms of synthesis, redox and thermal stability, they can be used successfully in photovoltaic cells as photosensitizers in energy and electron transfer reactions, potential laser dyes or organic transistor materials.

Synthesized naphthalene derivatives have thermal stability between 150-310 °C. Therefore, these naphthalene derivatives can be used in the fabrication of solar cells. The LUMO energy levels were determined by electrochemical analysis. The properties of synthesized naphthalene derivatives make them useful for application in optical and electronic materials.

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REFERENCES

1. P. Peumans, A. Yakimov and S.R. Forrest, *J. Appl. Phys.*, **93**, 3693 (2003).
2. N. Peyghambarian and R.A. Norwood, *Optics Photon. News*, **16**, 28 (2005).
3. C.W. Tang, *Appl. Phys. Lett.*, **48**, 183 (1986).
4. C.J. Brabec, N.S. Sariciftci and J.C. Hummelen, *Adv. Funct. Mater.*, **11**, 15 (2001).
5. M.T. Bernius, M. Inbasekaran, J. O'Brien and W. Wu, *Adv. Mater.*, **12**, 1737 (2000).
6. Y.Z. Wang, R.G. Sun, D.K. Wang, T.M. Swager and A. Epstein, *Appl. Phys. Lett.*, **74**, 2593 (1999).
7. J. Rostalski and D. Meissner, *Sol. Energy Mater. Sol. Cells*, **61**, 87 (2000).
8. M. Westphalen, U. Kreibig, J. Rostalski, H. Lüth and D. Meissner, *Sol. Energy Mater. Sol. Cells*, **61**, 97 (2000).
9. K. Takahashi, N. Kuraya, T. Yamaguchi, T. Komura and K. Murata, *Sol. Energy Mater. Sol. Cells*, **61**, 403 (2000).
10. M. Pfeiffer, A. Beyer, B. Plönnigs, A. Nollau, T. Fritzz, K. Leo, D. Schlettwein, S. Hiller and D. Wöhrle, *Sol. Energy Mater. Sol. Cells*, **63**, 83 (2000).
11. M. Hoffmann, K. Schmidt, T. Fritz, T. Hasche, V.M. Agranovich and K. Leo, in eds.: F. Kajzar and V. Agranovich, Multiphoton and Light Driven Multielectron Processes: Materials, Phenomena, Applications, NATO Advanced Research Workshop, Kluwer Dordrecht, The Netherlands, p. 123 (2000).
12. R.H. Friend, M. Granström, K. Petritsch, A.C. Arias, A. Lux and M.R. Andersson, *Nature*, **395**, 257 (1998).
13. C.C. Leznoff, Phthalocyanines, Properties and Applications, VCH, New York (1989).
14. M. Hiramoto, H. Fujiwara and M. Yokoyama, *Appl. Phys. Lett.*, **58**, 1062 (1991).
15. M. Hiramoto, H. Fukusumi and M. Yokoyama, *Appl. Phys. Lett.*, **61**, 2580 (1992).
16. H. Tröster, *Dyes Pigments*, **4**, 171 (1983).
17. M.J. Fuller and M.R. Wasielewski, *J. Phys. Chem. B*, **105**, 7216 (2001).
18. I. Yildiz-Oren, I. Yalcin, E. Aki-Sener and N. Ucarturk, *Eur. J. Med. Chem.*, **39**, 291 (2004).
19. H. Gilman, R. Adams, H.T. Clarke, J.B. Conant, C.S. Marvel, C.R. Noller and F.C. Whitmore, Organic Synthesis Collective, John Wiley & Sons, Inc, New York, edn 2, vol. 1, pp. 237–238 (1941).
20. H.M. Koepp, H. Wendt and H. Strehlow, *Z. Elektrochem.*, **64**, 483 (1960).
21. J.L. Bredas, R. Silbey, D.S. Boudreaux and R.R. Chance, *J. Am. Chem. Soc.*, **105**, 6555 (1983).
22. D. Uzun, M.E. Ozser, K. Yuney, H. Icil and M. Demuth, *J. Photochem. Photobiol. Chem.*, **156**, 45 (2003).
23. S. Alp, S. Erten, C. Karapire, B. Köz, A.O. Doroshenko and S. Icli, *J. Photochem. Photobiol. Chem.*, **135**, 103 (2000).