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Preparation of elastic polymer slices have the semiconductors properties for use in solar cells as a source of new and renewable energy

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ABSTRACT

The present work aimed to prepare elastic polymer slices that have semiconductors properties for use in solar cells based on charge transfer (CT) complexation. For this purpose, first six derivatives of 1,8–naphthalimide fluorescent dyes were synthesized. Secondly, the synthesized fluorescent dyes were complexed with *p*–chloranil acceptor via CT interaction in methanol solvent. The obtained CT complexes were dispersed in poly(methyl methacrylate) (PMMA) matrixes using methylene chloride solvent at room temperature. The obtained polymer sheets were characterized by several spectroscopic and physicochemical techniques, such as IR and UV–vis spectroscopies; and SEM technique. The microstructural and morphological changes occurred in the sheets of the PMMA matrix blended with the CT products were observed using the positron annihilation Doppler broadening (PADB) and the positron annihilation lifetime (PAL) techniques. Finally, the photostability and the direct current (DC) electrical characteristics as a function of the temperature for the CT products dispersed in PMMA matrixes have been studied.

1. Introduction

Due to the increasing global energy demand, limited fossil fuels, and increasing concern over environmental protection, the demand for finding and using sustainable clean energy sources has grown in the past decades. Solar energy is the most hopeful of providing inexhaustible energy because it is a kind of clean and renewable energy. One of the most promising classes of photovoltaic devices is dye-sensitized solar cells (DSSCs) which considered a 3rd generation solar cells. Recently, extensive researches were focused on the developing and designing DSSCs to be highly efficient, more low-cost, and more environmentally friendly [1–5]. Several metal-organic frameworks (MOFs), metal complexes, and thin films were investigated to be used in solar cells [6–9].

Fluorescent brighteners (FBs) are of interest as prospective polymer modifiers to obtain fluorescent polymers [10]. One important class of these brighteners is based on 1,8–naphthalimide derivatives [11–13]. These fluorescent dyes have found several applications especially in liquid crystals, laser active media, and solar energy collectors [14–23]. The chemistry of charge–transfer (CT) complexes is important subject for biologists and chemists. Due to the wide range of applications of CT complexes in various fields, they received a great deal of importance and attention. Such applications are electrical, magnetic, and optical conductivity, biological applications, quantitative estimations of drugs, and studying of drug-receptor mechanism [24–39]. The effect of reagents concentration, solvents, temperature and other parameters on the properties of the CT complexes are also intensively investigated [40–51].

As a part of our interest in studying the CT interactions of fluorescent dyes [52–58], the main aim of the present work is to prepare and characterize elastic polymer slices that have semiconductors properties for use in solar cells. The obtained polymer sheets are composed of poly (methyl methacrylate) (PMMA) and CT complexes derived from modified 1,8–naphthalimide fluorescent dyes and *p*-chloranil (CHL) ac-

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ceptor. The objectives of this work are achieved through the following steps:

- Syntheses:
  Six fluorescent alkoxy substituted 1,8-naphthalimide derivatives and their CT complexes with CHL acceptor are synthesized in methanol solvent at room temperature.
- Composite PMMA sheets:
  The obtained CT complexes are dispersed in poly(methyl methacrylate) (PMMA) matrix using methylene chloride solvent at room temperature.
- Characterization:
  The obtained polymer sheets are characterized by several spectroscopic and physicochemical techniques like IR and UV–vis spectroscopies; SEM; positron annihilation Doppler broadening (PADB) and positron annihilation lifetime (PAL).
- Electrical and photostability properties:
  The electrical and the photostability properties of the obtained polymer sheets at room temperature are investigated.

2. Experimental methods

2.1. Chemicals

All the chemicals were obtained from Aldrich, Merck and Fluka Chemical Companies and used as purchased. They were of high reagent grade and were used without modification.

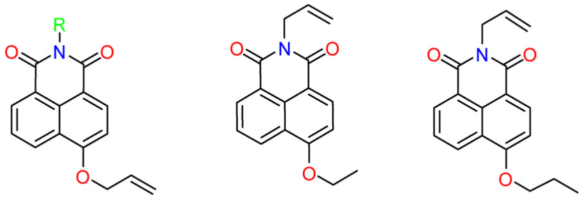
2.2. Procedures

2.2.1. Synthesis of the 1,8-naphthalimide derivatives

Six 1,8-naphthalimide derivatives (**1a**-**d**, **2** and **3**) with the chemical structures represented in Fig. 1 were synthesized according to methods previously described [59–63]. The choice of these fluorescent derivatives has been made on the basis of their good bleaching and photophysical properties [63,64]. The syntheses were done in a liquid/liquid two-phase system and the products (**1a**-**d**, **2** and **3**) were collected in high yield. The synthesized dyes were identified and characterized by their IR and ^{1}H NMR spectra, elemental analyses, and melting points.

2.2.2. Characterization of the synthesized dyes

For the 4-allyloxy-N-(n-butyl)-1,8-naphthalimide (**1a**); Yield 84%, m.p. 82–84 °C. FT-IR (KBr) cm^{-1}: 1682 ν_{as}(C=O), 1648 ν_a(C=O), 1463 ν(C=C), 1190 ν_{as}(C − N), 1079 ν_s(C–N). ^{1}H NMR (600 MHz, DMSO-*d$_6$*): δ = 0.98 (*t*, 3H, CH_3); 1.54 (*m*, 4H, 2 × CH_2); 3.26 (*t*, 2H, NCH_2); 4.56 (*m*, 2H, OCH_2); 5.20 (*m*, 2H, =CH_2); 5.82 (*m*, 1H, CH=); 7.60-6.68 (*m*, 2H, ArH); 8.56-7.94 (*m*, 3H, ArH). Analysis: $C_{19}H_{19}NO_3$ (309 g mol^{-1}); Calc. (%): C 73.78, H 6.16, N 4.52. Found (%): C 74.47, H 6.23, N 4.44.



1a-d **2** **3**

Key	R
1a	C_4H_9
1b	C_6H_{13}
1c	C_6H_4-CH_3 (*p*)
1d	C_6H_5

Fig. 1. Structures of the 1,8-naphthalimide derivatives.

For the 4-allyloxy-N-(n-hexyl)-1,8-naphthalimide (**1b**); Yield 87%, m.p. 63–65 °C. FT-IR (KBr) cm^{-1}: 1688 ν_{as}(C=O), 1650 ν_a(C=O), 1470 ν(C=C), 1189 ν_{as}(C − N), 1080 ν_s(C–N). ^{1}H NMR (600 MHz, DMSO-*d$_6$*): δ = 0.96 (*t*, 3H, CH_3); 1.48 (*m*, 8H, 4 × CH_2); 3.22 (*t*, 2H, NCH_2); 4.52 (*m*, 2H, OCH_2); 5.24 (*m*, 2H, =CH_2); 5.84 (*m*, 1H, CH=); 7.58–6.72 (*m*, 2H, ArH); 8.5–7.98 (*m*, 3H, ArH). Analysis: $C_{21}H_{23}NO_3$ (337 g mol^{-1}); Calc. (%): C 74.79, H 6.83, N 4.14. Found (%): C 74.01, H 6.72, N 4.23.

For the 4-allyloxy-N-(4-methylphenyl)-1,8-naphthalimide (**1c**); Yield 74%, m.p. 228–230 °C. FT-IR (KBr) cm^{-1}: 1694 ν_{as}(C=O), 1658 ν_a(C=O), 1467 ν(C=C), 1175 ν_{as}(C − N), 1072 ν_s(C − N). ^{1}H NMR (600 MHz, DMSO-*d$_6$*): δ = 2.24 (*s*, 3H, $ArCH_3$); 4.64 (*m*, 2H, OCH_2); 5.28 (*m*, 2H, =CH_2); 5.92 (*m*, 1H, CH =); 7.56–6.51 (*m*, 6H, ArH); 8.62-7.86 (*m*, 3H, ArH). Analysis: $C_{22}H_{17}NO_3$ (343 g mol^{-1}); Calc. (%): C 76.96, H 4.95, N 4.07. Found (%): C 77.56, H 5.04, N 4.15.

For the 4-allyloxy-N-phenyl-1,8-naphthalimide (**1d**); Yield 77%, m.p. 234–236 °C. FT-IR (KBr) cm^{-1}: 1698 ν_{as}(C=O), 1662 ν_a(C=O), 1471 ν(C=C), 1190 ν_{as}(C–N), 1080 ν_s(C–N). ^{1}H NMR (600 MHz, DMSO-*d$_6$*): δ = 4.78 (*m*, 2H, OCH_2); 5.42 (*m*, 2H, =CH_2); 6.06 (*m*, 1H, CH =); 7.63-6.78 (*m*, 7H, ArH); 8.62-8.08 (*m*, 3H, ArH). Analysis: $C_{21}H_{15}NO_3$ (329 g mol^{-1}); Calc. (%): C 76.61, H 4.55, N 4.26. Found (%): C 75.91, H 4.66, N 4.32.

For the N-allyl-4-ethoxy-1,8-naphthalimide (**2**); Yield 79%, m.p. 87–89 °C. FT-IR (KBr) cm^{-1}: 1685 ν_{as}(C=O), 1655 ν_a(C=O), 1466 ν(C=C), 1175 ν_{as}(C–N), 1070 ν_s(C–N). ^{1}H NMR (600 MHz, DMSO-*d$_6$*): δ = 1.32 (t, 3H, $OCH_2\underline{CH_3}$), 4.62 (t, 2H, OCH_2), 4.90 (d, 2H, NCH_2), 5.20 (*m*, 2H, =CH_2); 5.88 (*m*, 1H, CH =); 6. 90–8.47 (*m*, 5H, ArH). Analysis: $C_{17}H_{15}NO_3$ (281 g mol^{-1}); Calc. (%): C 72.59, H 5.33, N 4.99. Found (%): C 72.68, H 5.27, N 4.92.

For the N-allyl-4-propoxy-1,8-naphthalimide (**3**); Yield 81%, m.p. 88–90 °C. FT-IR (KBr) cm^{-1}: 1691 ν_{as}(C=O), 1653 ν_a(C=O), 1461 ν(C=C), 1180 ν_{as}(C–N), 1077 ν_s(C–N). ^{1}H NMR (600 MHz, DMSO-*d$_6$*): δ = 0.90 (t, 3H, $OCH_2CH_2\underline{CH_3}$), 1.74 (m, 2H, $OCH_2\underline{CH_2}$), 4.06 (t, 2H, OCH_2), 4.93 (d, 2H, NCH_2), 5.22 (*m*, 2H, =CH_2); 5.87 (*m*, 1H, CH=); 6.89-8.45 (*m*, 5H, ArH). Analysis: $C_{18}H_{17}NO_3$ (295 g mol^{-1}); Calc. (%): C 73.23, H 5.77, N 4.76. Found (%): C 73.28, H 5.83, N 4.68.

2.2.3. Synthesis of the CT complexes

An methanolic solution containing 1 mmol of each dye was mixed with an methanolic solution of CHL acceptor (1 mmol) and stirred for *ca.* 30 min at room temperature on a magnetic stirrer. The mixture was reduced to one-half by evaporation on a water bath. All the solid CT products were prepared by the same method. The CT products were filtered off and washed with methanol. Finally, the products were collected and dried in *vacuo* for 48 h [65–69].

2.2.4. Composite PMMA sheets

The solid CT complexes and PMMA grains were dissolved in methylene chloride and mixed well using a magnetic stirrer for 30 min. The homogenous mixture was poured into a glass petri dish and allowed to dry. The formed sheets were extracted carefully from dishes and were cut to rectangular shapes of rough dimensions 3 × 1 cm^3 [70].

2.3. Characterization techniques

2.3.1. Elemental analyses

Carbon, nitrogen, and hydrogen percentage in each CT product were determined using a CHN 2400 Perkin-Elmer Micro analyzer.

2.3.2. Electronic and Infrared spectra

The UV–vis. absorption spectra were collected in methanol solvent (200–800 nm) with a Perkin–Elmer Lambda 25 spectrophotometer with 1.0 cm quartz cells. The infrared (IR) spectra of the solid products were collected as KBr discs within the range of 400–4000 cm^{-1} on a Shimadzu FT-IR spectrophotometer.