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Research Papers

Synthesis and properties of fluorescent coumarin/ perylene-3,4,9,10-tetracarboxylic diimide hybrid as cold dye

Erisa Ferasat^{a,b}, Marzieh Golshan^{a,b}, Mehdi Salami-Kalajahi^{a,b,*}, Hossein Roghani-Mamagani^{a,b}

^a Faculty of Polymer Engineering, Sahand University of Technology, P.O. Box 51335-1996, Tabriz, Iran ^b Institute of Polymeric Materials, Sahand University of Technology, P.O. Box 51335-1996, Tabriz, Iran

| ARTICLE INFO | A B S T R A C T | | |
|--|--|--|--|
| <i>Keywords:</i> Cold dye Coumarin Fluorescence Perylene | Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) was modified by ethylenediamine to obtain perylene- 3,4,9,10-tetracarboxylic diimide (PTCDI). PTCDI as an initial core was used to bond coumarin derivatives. Successful conjugating of coumarin derivatives onto PTCDI was confirmed by Fourier-transform infrared spec- troscopy (FT-IR), proton nuclear magnetic resonance (¹ H NMR), X-ray diffraction (XRD), and field emission scanning electron microscope (FE-SEM). XRD peaks of various samples showed that the crystalline structure of PTCDA retained during the modification processes. The morphology of the nanoparticles by FE-SEM showed that the dyes were fibrillar. Fluorescence microscopy was used to evaluate the fluorescence properties of the dyes. In order to determine the amount of absorption and reflection in the near-infrared region, NIR test was used in both white and black fields. High absorption on a white background and high reflection on a black background indicated the transparency of the dye in the near-infrared region. The synthesized dye was identified and re- ported as a cold dye | | |

1. Introduction

Fluorescence colorants such as coumarin, perylene, and rhodamine often have advanced conjugate systems and a number of hybrid rings [1, 2]. One of the structural features of these dyes is relationship between molecular structure and the intensity of fluorescence, which leads to an increase in fluorescence efficiency [3]. Moreover, various factors including solvent, concentration, and temperature affect the fluorescence emission spectrum [4]. In addition to their importance as one of the brightest fluorescence dye groups, coumarins are one of most widely used fluorescence compounds [5,6]. The most important colors of coumarin fluorescence are reported to be yellow or green while they absorb and emit the light in most parts of visible spectrum. Important derivatives of coumarin dyes always have an electron-donor group in position 7, such as the dialkylamine, hydroxyl, or methoxy groups [7,8]. Coumarin compounds are widely used for production of fluorescent dyes due to their photophysical diversity and photochemical properties [8].

In recent years, perylene-3,4,9,10-tetracarboxylic diimide (PTCDI) is well-known as one the main source of vat dyes [9] and pigments [10]. PTCDI has a wide range of colors including red, vinaceous, violet,

brown, and black [11]. It is highly resistant to heat [12,13], light [14], and changes in environmental conditions [15]. Different PTCDI derivatives can be divided into two general categories [16,17]. The first group is derivatives obtained from the bonding of different groups to the nitrogen atoms in the imide groups [18] and the second category is the derivatives with the bonding of different groups to the bay sides [19]. Altering substituents can significantly change the properties of the dye. Not only PTCDI is often used as important dye in industries, but also has interesting features such as high photochemical stability, fluorescence quantum efficiency, and strong electron acceptance character [20].

The sun plays an important role in human life on earth. Solar energy heats objects such as buildings and cars [21]. This extra energy leads to an increase in indoor surface temperature and more energy consumption for air conditioning [22]. Increasing energy consumption to cool the interior has become a challenge for many years. The interaction of light with matter in the visible region causes the color in the matter [23]. Due to the very high reflection of sunlight, cold dyes effectively reduce the internal temperature. Cold dyes absorb less solar energy in infrared light and maintain a low surface temperature, transferring less energy to the interior and storing energy for air conditioning. There are significant

* Corresponding author. E-mail address: m.salami@sut.ac.ir (M. Salami-Kalajahi).

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Fig. 1. XRD patterns of PTCDA, PTCDI, HPTCDI-COUM, and DPTCDI-COUM.

differences in reports between cold dyes and regular dyes. Therefore, the use of cold dyes is an effective way to save energy for pleasant conditioning. Cold dyes can be organic and inorganic in nature [24]. Most commercial cold dyes are inorganic in nature and the organic cold dyes are very limited. Cold dyes include black dyes containing phthalocyanine, azo dyes, and a small number of perylene-based dyes such as lumogen, dye black 3, and dye black 32 [25].

Although various derivatives of perylene diimide have been synthesized and their properties have been investigated in various fields of fluorescence and NIR reflectance, the effect of coumarin derivatives on the structure of dye and hybridization with perylene chromophore has not been studied in scientific sources. The purpose of this work is to synthesize and investigate of optical and NIR reflectance properties of the hybrid perylene-coumarin dye. Perylene diimide derivatives have been prepared by modification of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) by ethylenediamine. Then, PTCDI has been used as a core, and coumarin derivative has been conjugated to synthesize a perylene-3,4,9,10-tetracarboxylic diimide-coumarin hybrid (HPTCDI-COUM). HPTCDI-COUM has been photodimerized to obtain another dye. Finally, NIR reflectance and photophysical behavior of synthesized dyes have been studied.

2. Experimental section

2.1. Synthesis steps

2.1.1. Synthesis of 4-methyl-7-(methoxy ethyl acetate) coumarin (MMEAC)

Suspension of 4-methylumbelliferone (COUM) (2 g, 11.35 mmol), anhydrous K_2CO_3 (8.5 g, 61.5 mmol), and ethyl bromoacetate (2.4 mL, 21.6 mmol) in THF (45 mL) was refluxed for 16 h at 60°C. After filtration, MMEAC was dried in a vacuum oven at 40°C and recrystallized in ethanol [26]. Reaction yield was calculated ~ 80% gravimetrically.

FT-IR of MMEAC (KBr, cm⁻¹, Fig. S4): (3076 CH str. C=CH), (2980, 2928 assym. str. CH₃, CH₂), (2872 sym. str. CH₃), (1759 C=O), (1606, 1508 str. C=C), (1423, 1386 CH₃, CH₂ bend), (1220 C-O ester), (1197 C-O lactone) [27,28].

¹H NMR of MMEAC (500 MHz, CDCl₃, δ/ppm, Fig. S5): 1.25 (t, 3H, h), 2.33 (s, 3H, b), 4.23 (q, 2H, g), 4.63 (s, 2H, f), 6.06 (s, 1H, a), 6.69 (d,

1H, d), 6.83 (d, 1H, e), 7.46 (d, 1H, c) [29].

2.1.2. Synthesis of 4-methyl-7-(carboxy methoxy) coumarin (MCMC)

MMEAC (1.0 g, 2 mmol) was dissolved in ethanol (25 mL). Then, 14 mL 5% NaOH solution was added to the reaction medium and the solvent was removed from the reaction medium. After dissolving the precipitate in water, 6 N HCl was added to the solution and allowed to form a white precipitate. Then, for purification, the precipitate was filtered using filter paper and separated from the solvent, and white-cream solid crystals were obtained by recrystallization from ethanol. Eventually, 4-methyl-7-(carboxy methoxy) coumarin was dried in a vacuum oven at room temperature for 24 h. The reaction for the preparation of MCMC is shown in Scheme S2 [26]. Reaction yield was calculated $\sim 60\%$ gravimetrically.

FT-IR of MCMC (KBr, cm⁻¹, Fig. S4): (3400-3500 str. OH), (3068 CH str. C=CH), (2987, 2916 assym. str. CH₃, CH₂), (1755 C=O), (1708 C=O), (1610, 1566, 1510 str. C=C), (1427, 1390 CH₃, CH₂ bend), (1253 C-O), (1147 C-O) [30,31].

¹H NMR of MCMC (500 MHz, CDCl₃, δ/ppm, Fig. S5): 2.39 (s, 3H, b), 4.78 (s, 2H, f), 6.06 (s, 1H, a), 6.21 (s, 1H, d), 6.98 (d, 1H, e), 7.69 (d, 1H, c) [32,33].

2.1.3. Synthesis of hybrid perylene-3,4,9,10-tetracarboxylic diimide/ coumarin (HPTCDI-COUM)

MCMC (2.4 g, 2 mmol), DCC (0.1 g, 0.48 mmol), and DMAP (0.02 g, 0.16 mmol) were dissolved in THF (25 mL). Then, PTCDI (section S2, 0.2 g, 42 mmol) was dissolved in THF (5 mL) and added dropwise to the reaction medium. The mixture was stirred at room temperature under nitrogen for 7 days. On completion of the reaction, the product was washed with diethyl ether (100 mL) and dried at 60°C for 24 h in a vacuum oven. Reaction yield was calculated ~ 70% gravimetrically. The reaction route is shown in Scheme 1.

FT-IR of HPTCDI-COUM (KBr, cm⁻¹, Fig. S1): 1680 (v^{as}N-C=O), 1660 (v^sN-C=O), (3068 CH str. C=CH), (2987, 2916 assym. str. CH₃, CH₂), (1726 C=O), (1708 C=O), (1610, 1510 str. C=C) [34,35].

¹H NMR of HPTCDI-COUM (500 MHz, DMSO, δ/ppm, Fig. S6): 5.8 (s, 1H, a), 2.0 (s, 3H, b), 6.0 (s, 1H, c), 4.5 (s, 2H, d), 3.7 (m, 4H, CH₂NH₂, f), 3.3 (m, 4H, CH₂NC=O, g), 7.9 (m, 8H, perylene, i).

¹³C NMR of HPTCDI-COUM (500 MHz, DMSO, δ /ppm, Fig. S7):



Fig. 2. FE-SEM images of PTCDI derivatives.

117.2 (<u>CH</u>, a), 20.8 (<u>CH</u>₃, b), 158.0 (<u>CCH</u>₃, c), 40.2 (<u>CH</u>, d), 72.4 (<u>C</u>-0, e), 134.8 (<u>CH</u>, f), 103.1 (<u>CH</u>, g), 123.4 (<u>CH</u>, i), 150.1 (<u>C</u>-O, h),67.1 (<u>OCH</u>₂, k), 168.6 (<u>C</u>=O, i), 36.4 (<u>CH</u>₂NH₂, m), 51.9 (<u>CH</u>₂NC=O, n), 159.3 (CH₂N<u>C</u>=O, o), 124.5, 130.9, 126.1 ((<u>C</u>) 1-naphthalene, r, q, s), 129.2 (<u>CH</u> (1-naphthalene, p).

2.1.4. Photodimerization of HPTCDI-COUM (DPTCDI-COUM)

Photodimerization of HPTCDI-COUM was performed under UV light at $\lambda > 310$ nm for 30 min with concentration of 0.2 mg mL⁻¹ at H₂SO₄ (Scheme 1). The degree of dimerization was measured using UV-VIS-NIR spectrum by Eq. (1) [36].

degreeof dimerization =
$$1 - \frac{A_t}{A_0}$$
 (1)

In this equation, A_0 and A_t are initial absorption and absorption after photodimerization, respectively.

2.2. Preparation of Dye

Nitrocellulose resin (64 *wt*. %), pigment (16 *wt*. %), and dye thinner (20 *wt*. %) were mixed and ball-milled for 5 h. Then, resultant paints were applied to Leneta checkerboard charts using a film applicator with a thickness of 120 μ m. This helped to prevent reflection of the substrate and only reflection of paint was detected. Evaluation of dyes reflectance on a highly reflective substrate (white substrate) and highly absorbent

substrate (black substrate) can qualitatively show the amount of reflection, transfer, and absorption of dye.

3. Results and discussion

3.1. Synthesis of hybrid dyes

The dyes were designed with a perylene diimide core covered by coumarin derivatives. XRD, UV-VIS-NIR, FS, FM, and FE-SEM analysis were used to evaluate and confirm PTCDI-cored MCMC in each step. FT-IR and ¹HNMR, and ¹³C NMR spectra of different dyes including COUM, MMEAC, MCMC, PTCDA, PTCDI, HPTCDI-COUM, and DPTCDI-COUM are depicted in Figs. S1-S7 and the most important peaks are mentioned in Section 2. Fig. 1 illustrates XRD patterns of different dyes including PTCDA, PTCDI, HPTCDI-COUM, and DPTCDI-COUM in the ranges of $10-70^{\circ}$ and $10-30^{\circ}$. In all patterns, sharp peaks due to the crystalline phase were observed in the structure. The peak at $2\theta=24.8^\circ$ is related to the stacking of PTCDI plates, which is also seen in other aromatic plate structures (201) [37]. Also, the peaks at $2\theta=27.7^\circ$ and 28.0° are related to the crystal structures (202) and (203) of perylene layers, respectively. Therefore, all dyes contain amorphous and crystalline phases [38,39]. The crystallinity index of dyes was obtained according to Eq. (2) [40].

$$Crystallinity(\%) = \frac{\text{Totalareaofcrystallinepeaks}}{\text{Totalareaofallpeaks}} \times 100$$
(2)



Fig. 3. Absorption and fluorescence spectra of synthesized colorants.

According to the results, crystallinity was obtained 85.7%, 62.9%, and 46.9% for PTCDA, PTCDI, and HPTCDI-COUM. Moreover, XRD patterns of the dyes showed that the characteristic peaks of PTCDI derivatives were similar to PTCDI that showed no significant change was occurred in nature of PTCDI. After photodimerization reaction of DPTCDI-COUM dye, the intensity of sharp crystalline peaks has decreased sharply and a wide peak has been formed in the range of 10- 26° .

Fig. 2 shows the FE-SEM images of PTCDA, PTCDI, HPTCDI-COUM, and DPTCDI-COUM. The structure of dyes is almost all rod-shaped with small sections and a glossy surface, which is due to the use of ultrasonic devices for better dispersion during sampling [41]. After the reaction of PTCDA with EDA, small aggregates were observed. Modification of PTCDI by coumarin derivatives changed the morphology of HPTCDI-COUM to fibrillar, and with the photodimerization reaction, the morphology of DPTCDI-COUM appeared as a lump. In fact, the change in structure causes the particles to become self-aggregating and out of the fibrillar state [42].

3.2. Photophysical properties of hybrid dyes

UV and FL spectra of samples are shown in Fig. 3. HPTCDI-COUM dye was exposed to UV light irradiation in H_2SO_4 for the photodimerization reaction. The presence of a coumarin derivative in the PTCDI imide region led to a photodimerization reaction with photon absorption at wavelengths above 310 nm [43]. Degree of dimerization of coumarin derivatives was obtained by reducing the absorption peak intensity in the range of 360-400 nm. Therefore, the degree of dimerization for HPTCDI-COUM was about 80% for the coumarin section according to Eq. (1). FL spectroscopy was used to evaluate the emission and quantum fluorescence efficiency of PTCDA, PTCDI, COUM, MCMC, HPTCDI-COUM, and DPTCDI-COUM samples. Quantum efficiency was obtained for samples based on perylene ($\lambda_{ex} = 460$ nm) and for coumarin derivatives ($\lambda_{ex} = 320$ nm) using Eq. (3) [44].

$$\Phi_s = \Phi_r \frac{m_s}{m_r} \left(\frac{\eta_s}{\eta_r} \right)^2 \tag{3}$$

In this equation, Φ_r is the quantum yield of the standard dye (Rh6G), $m_{\rm s}$ is the slope of the linear fit for the integrated fluorescence intensity of the fluorescent dye as a function of absorbence, and η_s and η_r are the refractive indices of the fluorescent dye and the standard solutions, respectively. The quantum fluorescence efficiencies of the samples were obtained 25, 17.2, 11.7, 5.2, 13.7, and 10.6% for PTCDA, PTCDI, COUM, MCMC, HPTCDI-COUM, and DPTCDI-COUM, respectively. The main feature of the perylene core is that it has a high tendency to aggregate through π - π bonds, which leads to the formation of molecular masses that increases the rate of charge transfer in the sample. All these properties are attributed to perylene chromophore. One of the features of this chromophore is the presence of perturbations in the absorption spectrum, which decreases the quantum efficiency by increasing the concentration. The reason for these properties is stacking through π - π bonds or larger molecular aggregations. By preventing π - π interactions, it is possible to achieve high concentrations with high fluorescence. There are two main ways to prevent π - π bond stacking. The first method is modification through positions 1, 6, 7, and 12 of the non-core region of perylene. By doing this modification, the tendency to π - π stacking and intermolecular dependence is reduced. Molecular isolation is another effective method to reduce the intermolecular π - π bonds in perylene diimide compounds, which is achieved by modifying the positions of 2, 8, 5, and 11 as ortho regions [45,46].

Fig. 4 displays fluorescence images of PTCDA, PTCDI, HPTCDI-COUM, and DPTCDI-COUM in powder mode. Due to the blue emission



Fig. 4. Fluorescence microscopy images of coumarin and PTCDI derivatives

Table 1

Decomposition temperatures of PTCDI and HPTCD-COUM.

| Sample | T ₁₀ | T ₅₀ |
|------------|-----------------|-----------------|
| PTCDI | 484.7 | 749.7 |
| HPTCD-COUM | 273.3 | 559.6 |

of coumarin derivatives and the red emission of perylene derivatives, the dyes were examined in two filters. According to the images, the stability of the fluorescence emission of different samples in blue and red filters is quite evident. After photodimerization, the DPTCDI-COUM sample showed poor emission in the red filter.

3.3. Thermal stability

According to Figure S8, PTCDI and HPTCDI-COUM dyes were examined by thermogravimetric analysis (TGA). Table 1 shows T_{10} and T_{50} of PTCDI and HPTCD-COUM. According to the results, PTCDI showed T_{10} of 484.7°C whereas after hybridization with coumarin, T_{10} was decreased to 273.3°C. However, both dyes showed T_{50} higher than 550°C which confirmed thermal stability of synthesized hybrid dye. Due to the thermal stability of these dyes, the use of these compounds in various fields will increase in the future [47].

3.4. NIR properties of hybrid dyes

Fig. 5 illustrates UV-Vis-NIR reflectance of the PTCDI and HPTCDI-COUM. In this research, two different optically substrates, black and white, have been used to investigate the amount of radiation transmission. These substrates play a key role in the classification of PTCDI and HPTCDI-COUM in the NIR region. Howbeit, the dyes with similar structures illustrate different reflectance in the UV-Vis-NIR region. The difference in a reflection in the visible region is due to the difference in color of the colorants and the difference in reflection in the NIR region can be attributed to different crystal structures [23,24]. In view of the above discussion, PTCDI and HPTCDI-COUM indicate absorption in visible region (400-700 nm) due to the nature of dyes. However, in NIR region (700-1000 nm) PTCDI shows high reflectance in white substrate and low reflectance in the black substrate; so, it is NIR transparent. In addition, integrals of UV-Vis-NIR curves in three regions are studied and the data are summarized in Table 2. PTCDI had a reflection of 57% in range of 700-1000 nm and showed good transparency, while HPTCDI-COUM showed a weaker reflection. According to the results, both synthesized dyes can be used as cold dyes in the construction and military industries, depending on the required shade. For both dyes, a near-zero reflection in the visible region was reported due to strong adsorption by the synthesized dyes. It is noteworthy that the transparency is more pronounced for the synthesized dyes, which is probably due to the regular and fibrillar structure of the synthesized sample. Furthermore, dyes were examined under an IR lamp. The results showed that the color of dyes changed from dark to white (Figure S9).

4. Conclusions

Herein, a perylene-coumarin hybrid dye with a perylene core was prepared. To prepare a coumarin derivative, 4-methyl-7-(carboxy methoxy) coumarin was prepared by acid hydrolysis from 4-methyl-7-(methoxy ethyl acetate) coumarin. XRD patterns of different samples showed that the crystal structure of PTCDI derivatives was not destroyed during various purification processes, after the photodimerization reaction, and sample preparation. In DPTCDI-COUM, the intensity of sharp crystalline peaks was drastically reduced and a wide peak was formed in the range of 10-26°. The fluorescence properties of the synthesized dyes and their potential application as cold dyes were investigated. Quantum fluorescence efficiency of samples was obtained 25, 17.2, 11.7, 5.2, 13.7, and 10.6% for PTCDA, PTCDI, COUM, MCMC, HPTCDI-COUM, and DPTCDI-COUM, respectively. According to results, properties of synthesized NIR dyes depend on the nature of nitrogen exchange, and with the change in substitutions, the amount and type of NIR properties of dyes were changed. The results of NIR spectrum of the synthesized dyes showed that the synthesized dyes belong to transparent category in NIR region.

Data availability

The raw/processed data required to reproduce these findings cannot



Fig. 5. Reflectance UV-Vis-NIR integral of PTCDI and HPTCDI-COUM.



Scheme 1. Synthesis mechanism and photodimerization reaction of HPTCDI-COUM.

be shared at this time as the data also form part of an ongoing study. Supporting information

Materials, Instrumentation, FT-IR, 1H NMR, TGA, and IR lamp results.

CRediT authorship contribution statement

Erisa Ferasat: Formal analysis, Investigation, Investigation, Writing – original draft, Visualization. Marzieh Golshan: Validation, Formal analysis, Writing – original draft, Visualization. Mehdi Salami-Kalajahi: Conceptualization, Validation, Resources, Writing – review & editing, Visualization, Supervision, Funding acquisition. Hossein

Roghani-Mamaqani: Conceptualization, Validation, Resources, Visualization, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.materresbull.2021.111500.

Table 2

Percentage of reflection of PTCDI and HPTCDI-COUM in different areas.

| Sample | 700-1000 (nm) | 1000-1500 (nm) | 1500-2500 (nm) |
|-----------------|----------------|----------------|----------------|
| White substrate | 26819 | 41188 | 55577 |
| PTCDI | 15444 | 40909 | 60811 |
| HPTCDI-COUM | 12972 | 36754 | 58634 |
| Sample | Reflection (%) | Reflection (%) | Reflection (%) |
| PTCDI | 57% | 99% | 1% |
| HPTCDI-COUM | 48% | 89% | 1% |
| Sample | 700-1000 (nm) | 1000-1500 (nm) | 1500-2500 (nm) |
| Black substrate | 1981 | 3297 | 8223 |
| PTCDI | 4626 | 7684 | 15321 |
| HPTCDI-COUM | 2610 | 5180 | 12914 |
| Sample | Reflection (%) | Reflection (%) | Reflection (%) |
| PTCDI | 2.3% | 2.3% | 1.8% |
| HPTCDI-COUM | 1.3% | 1.5% | 1.5% |
| | | | |

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