

Synthesis of a conjugated molecular triad based on 9,9-dioctyl-9H-fluorene for fluorescence sensing to determine mesotrione

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Abstract:

A conjugated molecular triad based on pyrene and 9,9-dioctyl-9H-fluorene has been successfully synthesised via the Suzuki cross-coupling reaction with yield of 48%. In this polymerization, the Pd(PPh₃)₄ has been used as the catalytic in the presence of K₂CO₃ as base in a mixture of toluene/ethanol/H₂O at 80°C under N₂. The chemical structures of the conjugated molecules were determined via Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (¹H-NMR) that proved the chemical structure of 1,1'-(9,9-dioctyl-9H-fluorene-2,7-diyl)dipyrene. The optical properties of the molecules were investigated via UV-Vis in different concentration that exhibited the maximum absorption of 340 nm. The conjugated molecular triad also have been investigated by fluorescence spectroscopy that showed a mission peak at 475 nm under the excitation of 350 nm of wavelength. In addition, the 1,1'-(9,9-dioctyl-9H-fluorene-2,7-diyl)dipyrene exhibited a fluorescence quenching as a chemosensor in the presence of mesotrione, a nitroaromatic herbicide. This phenomenon proved the efficient energy and electron transfer from a photo-excited pyrene moiety to the ground state electron-deficient mesotrione as a result of Forster resonance energy transfer (FRET) mechanism..

Keywords: chemosensor, conjugated molecular, mesotrione, nitroaromatic herbicide, pyrene.

Classification numbers: 2.2, 2.3

1. Introduction

Recently, nitroaromatic compounds (NACs) have been widely used in various industrial chemicals and pharmaceuticals such as in the synthesis of herbicides, dyes, explosives, and other intermediates [1-4]. NAC contamination in surface water, groundwater, and soil can cause serious health problems in living organisms [5-7]. Moreover, because NACs contain one or more electron-withdrawing nitro-groups, they slowly biodegrade in the environment [4, 5]. Most NACs are known as mutagenic and carcinogenic agents towards humans and cause the formation of methemoglobin upon acute exposure [5]. Therefore, tracing these compounds in the environment is of great importance.

Some advanced methods such as high-performance liquid chromatography (HPLC), gas chromatography coupled mass spectrometry (GC-MS), ion-mobility spectroscopy (IMS), and surface-enhanced Raman spectroscopy (SERS) have been used for the detection of NACs [8, 9]. Although most of these methods are capable of detecting low concentrations of NACs, they usually require complicated equipment and skilled operators, are time consuming, and lack portability. Recently, optical detection

methods have emerged as a powerful alternative because of their low cost, high sensitivity and selectivity, and good portability [10]. Notably, fluorescent sensing has great promise for wide application due to its simplicity, ease of visualisation, and quick responses [11]. Thus, this method has become the focus of discussion in this research.

A wide range of fluorescent-based NAC sensors have been designed including organic dyes, conjugated polymers, quantum dots, metal-organic frameworks, and nanomaterials [12-26]. In the fluorescence method, the main interactions responsible for fluorescence quenching are photo-induced electron transfer and Forster resonance energy transfer [10]. L.L. Zhou, et al. (2016) [11] reported the synthesis of conjugated polymers based on benzo[5]helicene via the Sonogashira coupling, Suzuki coupling, and Yamamoto homocoupling reactions for the detection of NACs. A.S. Tanwar, et al. (2019) [24] reported the synthesis of 9,9-bis(6-bromohexyl)-2-phenyl-9H-fluorene and 9,9-bis(6-bromohexyl)-9H-fluorene via the Suzuki polymerization coupling reaction as a fluorescence sensor to detect picric acid. In addition, V. Saini, et al. (2020) [27] reported the synthesis of a compound based on benzimidazo-quinazolinone and pyridinium,

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named 1-(2-(6-oxobenzo [4,5]imidazo [1,2-*c*]quinazolin-5(6H)-yl)ethyl)pyridin-1-ium bromide (BZQZPy), for detection of 2,4,6-trinitrophenol (TNP) in aqueous media. The compound BZQZPy is highly sensitive and selective towards TNP with a high Stern-Volmer constant of $1.53 \times 10^4 \text{ M}^{-1}$ and a low detection limit of 20 nM [28, 29].

During our research studies involving the synthesis of fluorescence sensors, we became interested in pyrene and its derivatives due to their good photophysical properties, structural characteristics, and high chemical stability. Pyrene has a large planar conjugated aromatic system, which allows for the formation of strong π - π interactions with NACs [10, 30-33]. Moreover, with its remarkable electron donor ability, pyrene can form a non-fluorescent charge transfer complex with electron-deficient molecules such as NACs [30]. In addition, fluorene is not only a strong electron donor moiety, but also exhibits a high fluorescent quantum yield due to the rigidity of the molecule's structure [34]. The alkyl group at the 9 position of fluorene could prevent self-quenching through π - π interaction and enhance the solubility of its derivatives in a common organic solvent [6, 35]. With the fascinating properties of pyrene and fluorene, we expect their incorporation to create a promising compound for fluorescence sensors in the detection of NACs.

In this paper, we report the synthesis of a conjugated oligomer based on pyrene and fluorene via the Suzuki coupling reaction. The structural characteristics of obtained oligomer are analysed via FTIR and $^1\text{H-NMR}$ spectroscopy. Then, its photophysical properties and fluorescence quenching response to NACs are investigated via UV-visible absorbance and photoluminescence (PL) spectroscopy for sensing applications.

2. Experimental design

2.1. Materials

N-bomosuccinimide (99%) and pyrene (98%) were purchased from Acros Organic. Mesotrione (98%), 2,2'-(9,9-dioctyl-9H-fluorene-2,7-dityl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (DFTD, 99%) and Tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$, 99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Potassium carbonate (K_2CO_3 , 99%) was purchased from Acros and used as received. Chloroform (CHCl_3 , 99.5%), dimethylformamide (DMF, 99%) and toluene (99.5%) were purchased from Fisher/Acros and dried using molecular sieves under N_2 . Dichloromethane (DCM, 99.8%), absolute ethanol (99%), and hexane (99%) were purchased from Fisher/Acros.

2.2. Characterisation

$^1\text{H-NMR}$ spectroscopy was performed in deuterated chloroform (CDCl_3), with TMS as an internal reference, on a Bruker Avance 500 MHz. FTIR spectra were collected as the average of 64 scans with a resolution of 4 cm^{-1} , which were recorded from a KBr disk on an FTIR Bruker Tensor 27.

UV-visible absorption spectra of the compounds were recorded on an Agilent 8453 spectrometer over a wavelength

range of 190-1100 nm. Fluorescence spectra of the compound in solution were measured on a Varian Cary Eclipse fluorescence spectrometer with slit widths of 5 nm.

2.3. Synthesis of 1-bromopyrene

Pyrene (1.00 g, 4.94 mmol) was added to 20 ml of anhydrous DMF that was charged in a 100-ml two-neck round-bottom flask. The mixture was cooled to 0°C , followed by the slow addition of *N*-bromosuccinimide (NBS) (0.97 g, 5.43 mmol) to the reaction mixture. Then, the reaction mixture was stirred and warmed to room temperature overnight. To end the reaction, the reaction was quenched by the addition of ice water and extracted with chloroform (60 ml). The mixture was washed with brine (150 ml), dried over anhydrous K_2CO_3 , and isolated by filtration. Then, the solvent was evaporated under vacuum pressure using a rotary evaporator. The obtained product was precipitated with cold hexane to obtain a pure white powder. Finally, the pure compound was dried under vacuum in an oven at 50°C to obtain a white powder (yield=94%). $^1\text{H-NMR}$ (500 MHz, CDCl_3), δ (ppm): 8.45 (d, $J=8.5 \text{ Hz}$, 1 H), 8.25-8.21 (m, 3 H), 8.19 (s, 1 H), 8.07-8.01 (m, 4 H).

2.4. Synthesis of 1,1'-(9,9-dioctyl-9H-fluorene-2,7-diyl)dipyrène (DFDP)

In a two-neck round-bottom flask, $\text{Pd}(\text{PPh}_3)_4$ (0.07 g, 0.06 mmol) and K_2CO_3 (138.2 mg, 3.16 mmol) were added into a mixture of toluene/ethanol/ H_2O (10:2:1.5, v/v), then 1-bromopyrene (390.93 mg, 1.39 mmol) and DFTD (406.13 mg, 0.63 mmol) were added to the solution under nitrogen flux. The reaction mixture was degassed by three freeze-pump-thaw cycles to remove air and moisture in reaction. Then reaction was carried out at 80°C under N_2 for 19 h. After the reaction mixture was cooled to room temperature, the mixture was extracted with chloroform three times ($3 \times 20 \text{ ml}$) and the combined organic layers were washed with 10% NaCl (150 ml), dried over K_2CO_3 , and the products were purified by column chromatography on a silica gel column using a mixture of hexane and DCM (V/V = 5:1). Finally, the products were dried in a vacuum oven at 50°C to obtain a light-yellow powder (DFDP, yield=48%).

$^1\text{H-NMR}$ (500 MHz, CDCl_3), δ (ppm): 8.27 (m, 4H), 8.21 (d, $J=7.6 \text{ Hz}$, 2H), 8.18 (d, $J=7.5 \text{ Hz}$, 2H), 8.14-8.09 (m, 6H), 8.05-8.00 (m, 4H), 7.98 (d, $J=8.0 \text{ Hz}$, 2H), 7.67 (m, 4H), 2.10 (t, 4H), 1.28-1.08 (m, 24H), 0.81 (t, 6H).

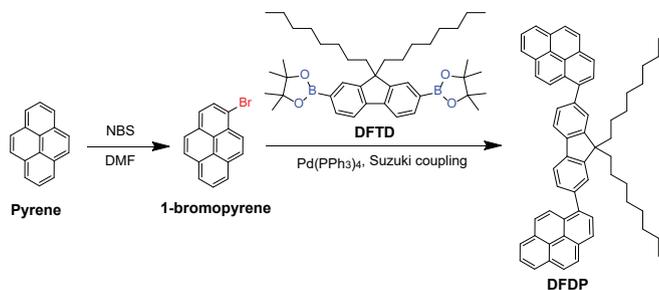
3. Results and discussion

3.1. Synthesis and oligomer structure

Pyrene and fluorene derivatives generally demonstrate promising optical properties as they both have an extensive π -system and high electron symmetry, which help improve fluorescence efficiency. Pyrene-fluorene hybrids are good potential materials for fluorescence chemosensor applications.

The synthetic route of DFDP is presented in Scheme 1. Here, 1-bromopyrene and DFDP were synthesized according

to the procedure reported in [36]. As shown in Scheme 1, the bromination reaction between pyrene and NBS at room temperature overnight afforded 1-bromopyrene with a yield of 94%. Then, the Suzuki reaction of 1-bromopyrene and DFTD was reacted using Pd(PPh₃)₄ as the catalyst in a mixture of toluene/ethanol/H₂O at 80°C under N₂ for 19 h, which was transformed into DFDP with a yield of 48%. After being purified by column chromatography, the compound DFDP was characterised by FTIR and ¹H-NMR spectrometry to confirm its chemical structure.



Scheme 1. Synthetic route for the conjugated oligomer DFDP.

DFDP was structurally elucidated by FT-IR analysis. The FT-IR spectrum of DFDP was scanned in the frequency region of 400-4000 cm⁻¹ using an infrared spectrometer by employing the KBr pellet technique. In Fig. 1, the FTIR spectrum indicated bands in the range of 2840-2975 cm⁻¹ related to -CH₂ and -CH₃ stretching, and the peak at 1461 cm⁻¹ related to the -CH₃ bending of octyl brand chain. Meanwhile, the C=C stretching mode of the aromatic ring was present in the range 1620-1570 cm⁻¹ and the band at 837 cm⁻¹ was attributed to C-H bending. Thus, FT-IR spectroscopy was able to determine the chemical functional groups present within DFDP. To further investigate DFDP's chemical structure, ¹H-NMR spectroscopy was also used.

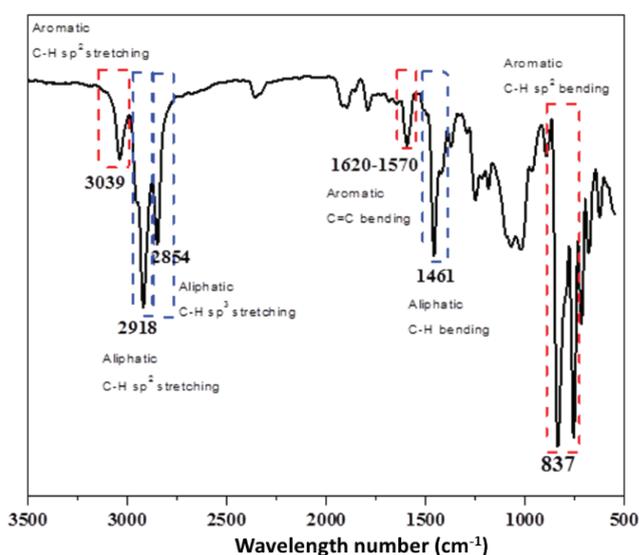


Fig. 1. FTIR spectrum of DFDP.

Figure 2 exhibits the ¹H-NMR spectrum of the obtained oligomer, which revealed characteristic peaks corresponding to the oligomer structure. In the ¹H-NMR spectrum of DFDP, signals observed from 0.8 to 2.1 ppm were assigned to the alkyl side chains. The peak at 7.67 ppm was attributed to the proton at position *x* in the fluorene unit and the proton at position *a* in the pyrene unit. However, the broad multiplets in the ranges 7.98 to 8.09 ppm and 8.18 to 8.3 ppm in the aromatic region corresponded to protons in the pyrene ring. In addition, the multiplets peak from 8.1 to 8.15 ppm were assigned to the protons of the pyrene unit at position *c* and to the fluorene unit at positions *y* and *j*. The results acquired from FT-IR and ¹H-NMR spectrometers were analysed for useful information about the structure and ultimately to confirm the successful synthesis of the conjugated oligomer DFDP.

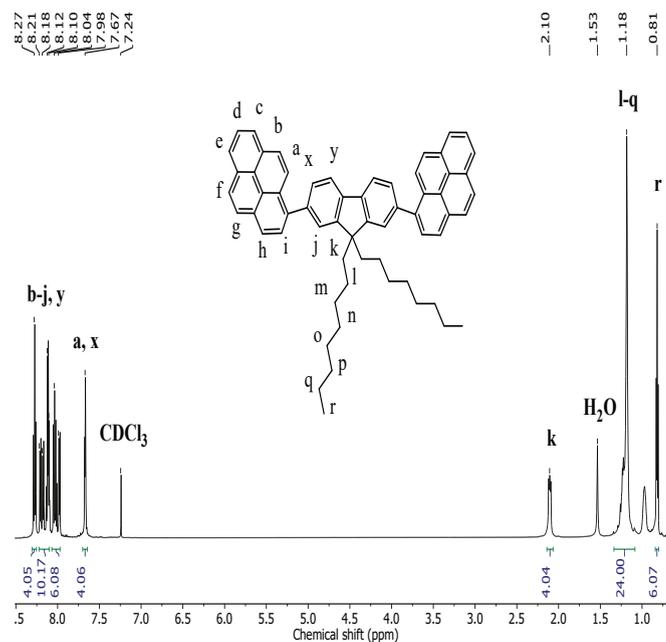


Fig. 2. ¹H-NMR spectrum of conjugated oligomer DFDP.

3.2. Optical properties

Figure 3A shows the UV-Vis absorption spectra of the oligomer DFDP in a dilute solution. The UV-Vis absorption of DFDP was investigated in CHCl₃ at different concentrations (5, 10, 20, and 30 μM). An absorption band emerged at 340 nm for the oligomer DFDP, while wavelengths from 400 nm onwards had no absorption. The absorption band at 340 nm was assigned to the electronic transition of fluorene and pyrene. Based on the Lambert-Beer law, the molar absorption coefficient ε of DFDP at a maximum wavelength of 340 nm is estimated to be 33525 M⁻¹cm⁻¹.

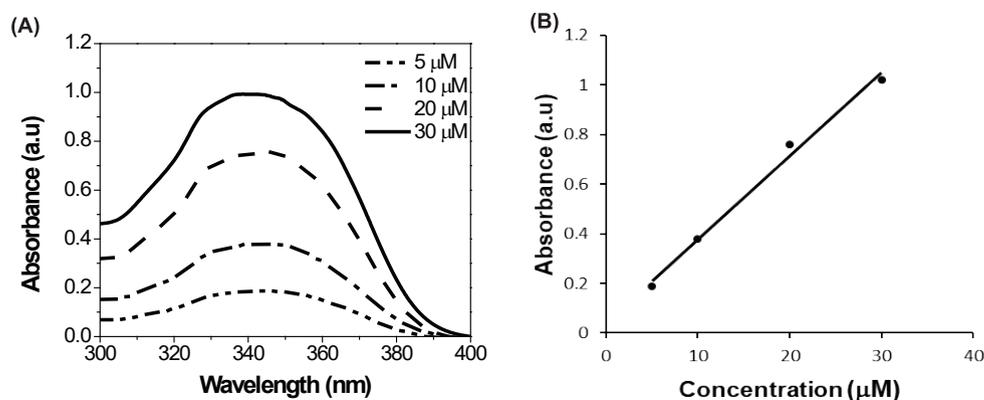


Fig. 3. (A) UV-vis absorption spectra of DFDP in different concentrations of CHCl_3 with a path length of 1 cm; (B) calibration curve of DFDP measured at λ_{max} .

3.3. Fluorescence quenching studies with mesotrione in solution

To obtain the quenching efficiencies of DFDP in the presence of a NAC, experiments using a microliter syringe were carried out in which the herbicide mesotrione was gradually added into oligomers dissolved in CHCl_3 ($C_M = 1.0 \mu\text{l}$). From Fig. 4, the fluorescence intensities of the oligomer DFDP in solution gradually decreased with the increase of mesotrione concentration (0-7.5 mM), which can be clearly observed under the illumination of UV light by the naked eye. The fluorescence quenching can be explained by the structure of DFDP, which has a conjugated, electron-rich structure with significant electron-donating capabilities to NACs. The observed quenching process of DFDP was the result of the efficient energy and electron transfer from a photo-excited pyrene moiety to the ground state electron-deficient mesotrione.



Fig. 4. Fluorescence quenching of DFDP in CHCl_3 (1 μM) upon addition of mesotrione (0-7.5 mM).

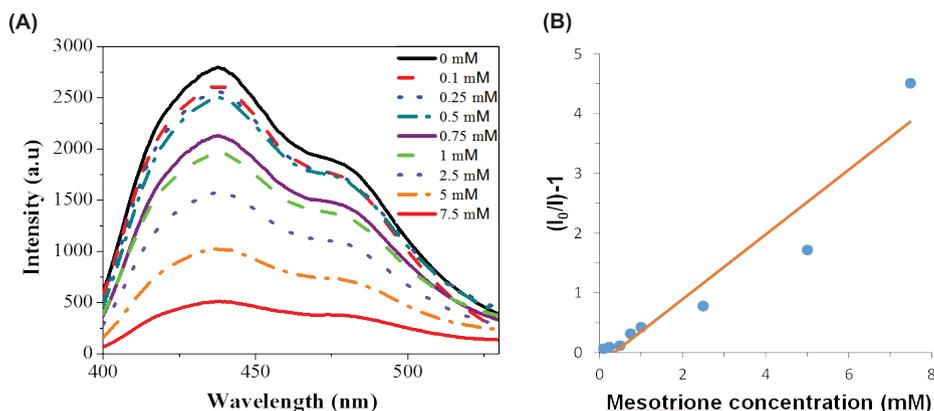


Fig. 5. (A) Fluorescence emission spectra of DFDP in CHCl_3 (1 μM) with increasing concentration of mesotrione and (B) the corresponding Stern-Volmer plot of DFDP.

To gain a complete understanding of the fluorescence quenching efficiency induced by mesotrione on DFDP, the fluorescence emission spectrums was evaluated using the Stern-Volmer equation:

$$\frac{I_0}{I} = 1 + K_{SV}C_A$$

where I_0 and I are noted as the fluorescence intensities in the absence and presence of the analyte (quencher, A), respectively; C_A denotes the molar concentration of the analyte, and K_{SV} denotes the Stern-Volmer quenching constant. Fig. 5B shows the linear responses of $[(I_0/I)-1]$ vs. the concentration of the nitroaromatic herbicide mesotrione with a correlation coefficient of 0.92, which determines the quenching efficiency of conjugated oligomer DFDP. The calculated Stern-Volmer constant (K_{SV}) of DFDP was 544 M^{-1} with the detection limit (DL) of mesotrione down to 0.2 mM based on the standard method reported.

4. Conclusions

In this research, a conjugated oligomer based on pyrene and fluorene, DFDP, was successfully synthesised at a 48% yield via the Suzuki cross-coupling reaction. The obtained oligomer DFDP was tested to trace the nitroaromatic herbicide mesotrione with a calculated Stern-Volmer constant K_{SV} of 544 M^{-1} and a

detection limit of 0.2 mM. The results prove that the pyrene-based conjugated oligomer could be a promising candidate for real life applications like a fluorescence sensor of NACs.

CRedit author statement

Thao Phuong Le Nguyen: Conceptualization, Methodology, Formal analysis; Thao Thanh Bui: Conceptualization, Methodology, Formal analysis; Bao Kim Doan: Software, Data curation, Validation; Linh Phuong Bui: Software, Data curation, Validation; Tam Hoang Luu: Visualization, Investigation; Chau Duc Tran: Investigation; Tung Viet Tuan Tran: Software, Data curation, Validation; Tsutomu Yokozawa: Writing- Reviewing and Editing; Ha Tran Nguyen: Project administration.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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