Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2022, **32**, 523–526

Mendeleev Communications

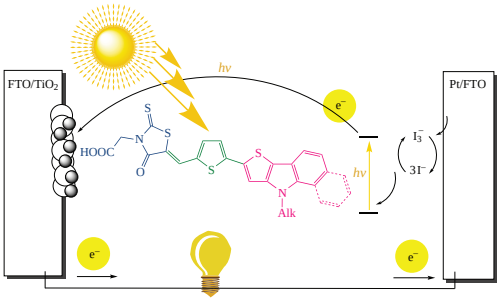
New thieno[3,2-*b*]indole conjugates with 5-(methylene)rhodanine-3-acetic acid in dye-sensitized solar cells

Alexander S. Steparuk,[a] Roman A. Irgashev,*[a,b] Ekaterina F. Zhilina,[a] Viktor V. Emets,[c] Vitaly A. Grinberg,[c] Ekaterina V. Tekshina,[d] Ekaterina V. Belova,[e] Petr I. Lazarenko,[f] Nikita M. Tolkach,[f] Gennady L. Rusinov[a,b] and Sergey A. Kozyukhin[d,g]

[a] *I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 620108 Ekaterinburg, Russian Federation. E-mail: irgashev@ios.uran.ru*
[b] *Institute of Chemical Engineering, Ural Federal University, 620002 Ekaterinburg, Russian Federation*
[c] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russian Federation*
[d] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*
[e] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[f] *National Research University of Electronic Technology, 124498 Zelenograd, Moscow, Russian Federation*
[g] *Moscow Institute of Physics and Technology, 141701 Dolgoprudny, Moscow Region, Russian Federation*

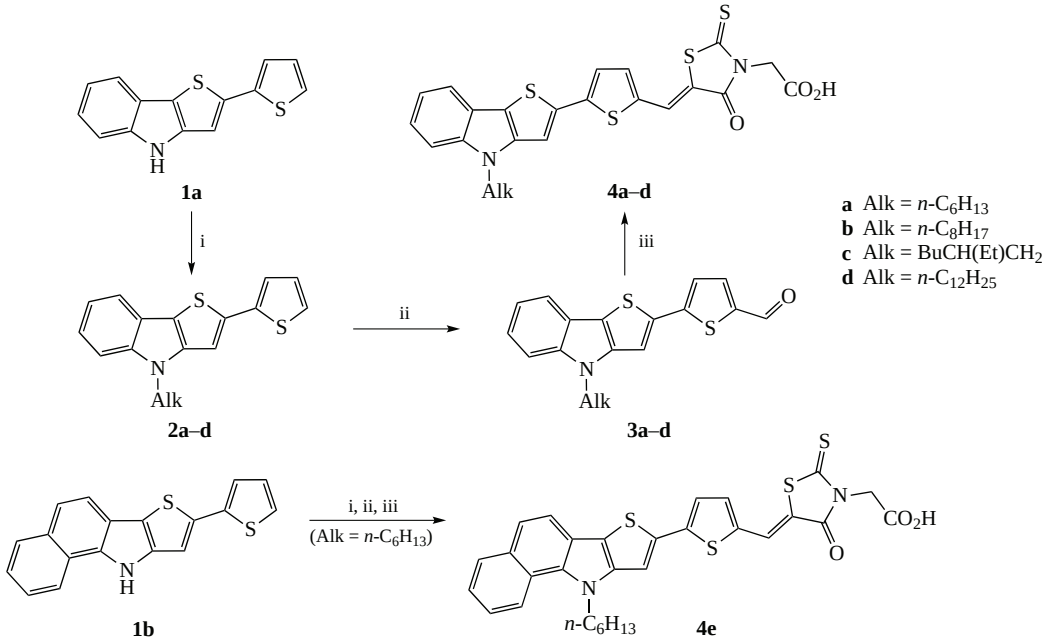
DOI: 10.1016/j.mencom.2022.07.030

Five new dyes with D–π–A structure bearing 5-(methylene)-rhodanine-3-acetic acid as an acceptor-anchoring part and thieno[3,2-*b*]indole or benzo[*g*]thieno[3,2-*b*]indole as an electron-donating part were synthesized and applied as photosensitizers for dye-sensitized solar cells (DSSCs). In addition, thermal stability, optical and electrochemical properties of these dyes were investigated. The highest PCE value of 1.09% (J_{sc} = 3.01 mA cm^{-2}, V_{oc} = 0.53 V, FF = 0.69) was achieved for DSSC based on benzo[*g*]thieno[3,2-*b*]indole dye under AM 1.5G irradiation.



Keywords: thieno[3,2-*b*]indoles, rhodanine-3-acetic acid, metal-free dyes, D–π–A structure, dye-sensitized solar cells.

Over the past three decades, the technology of dye-sensitized solar cells (DSSCs) has attracted considerable attention due to the broad prospects of its application for the development of high-performance photovoltaic devices.[1–3] Indeed, the basic model of DSSC, firstly described by Grätzel and O'Regan yet in 1991, represents inexpensive and easily manufacturable device, including photoanode with a thin layer of nanocrystalline TiO_2 or another wide-gap semiconductor, organic dye-sensitizer adsorbed onto the TiO_2 layer, electrolyte, and counter electrode.[4] Thus, dye-sensitizer is one of the key components in the structure of DSSCs, since its nature primarily provides the light-harvesting ability of these devices, which directly affected their photovoltaic performance.[5] Metal-free organic dyes containing donor, π-linker, and acceptor fragment in their molecules, that is D–π–A structure, have found to be attractive as the photosensitizers for DSSCs.[6,7] This is primarily due to a wide range of synthetic tools for the construction of metal-free dyes that provide turnability of their optical and electrochemical properties,[8] and ability to elaborate facile procedures for their preparation and purification. In general, the synthetic approaches towards push-pull dyes often involve transition-metal-catalyzed processes, *e.g.* Pd-catalyzed reactions, used to link single molecular fragments for the stepwise construction of π-conjugated scaffold of the target dye.[9,10] At the same time, the construction of push-pull molecules seems to be also attractive using compounds bearing several π-linked fragments of the D–π–A system, and methods allowing one to obtain directly these intermediates, excluding transition-metal-catalyzed processes.[11] In this context, we have previously described convenient approaches towards 2-(hetero)aryl-substituted thieno[3,2-*b*]indoles (TIs),[12,13] when 2-(thiophen-2-yl)thieno[3,2-*b*]indole was used to prepare D–π–A dyes containing thieno[3,2-*b*]indole as an electron-donating part and 2-cyanoacrylic acid as an electron acceptor-anchoring part, for DSSC application.[14] It should be noted that 2-cyanoacrylic acid is the most popular acceptor-anchoring unit used in the design of metal-free D–π–A photosensitizers.[15] Nevertheless, a number of other molecular moieties were suggested as the acceptor-anchoring units to form metal-free D–π–A dyes for DSSCs.[15,16] Among them, 5-(methylene)rhodanine-3-acetic acid (MRAA) fragment was also applied in the structure of D–π–A photosensitizers as an acceptor-anchoring part in the combination with different electron-donating moieties, such as phenothiazine,[17] indole,[18,19] indoline,[20] triarylamines,[21–23] 4-dimenylaminophenyl[24] and 2,4,6-trimethoxyphenyl.[25] It is important that the presence of CO_2H group in the structure of MRAA moiety provided effective binding MRAA-based photosensitizers onto the TiO_2 surface, as well as for dyes based on 2-cyanoacrylic acid. Moreover, dyes bearing both MRAA and 2-cyanoacrylic acid acceptors can be readily formed by the condensation of the appropriate π-conjugated aldehydes with commercially available rhodanine-3-acetic acid or 2-cyanoacetic acid, respectively.



Scheme 1 *Reagents and conditions*: i, AlkBr, NaH, DMF, room temperature, 24 h; ii, $Me_2NC(O)H$, $POCl_3$, $CHCl_3$, room temperature, 48 h; iii, rhodanine-3-acetic acid, pyrrolidine, AcOH, 120 °C, 1 h.

Herein, we report the photovoltaic properties study of DSSCs based on new D–π–A dyes **4a–e** bearing MRAA as an acceptor-anchoring part, and thieno[3,2-*b*]indole **4a–d** or benzo[*g*]-thieno[3,2-*b*]indole **4e** as an electron-donating part (Scheme 1). In turn, dyes **4a–d** and **4e** were readily synthesized in three steps starting from known[10] 2-(thiophen-2-yl)thieno[3,2-*b*]indole **1a** and 8-(thiophen-2-yl)benzo[*g*]thieno[3,2-*b*]indole **1b**, respectively (for details, see Online Supplementary Materials). In addition, optical and electrochemical characteristics of the obtained dyes as well as their thermal stability were elucidated in the current study.

Thermal degradation of dyes **4a–e** was investigated using thermogravimetric analysis under air flow (Figure 1 and Table S2 of Online Supplementary Materials). All dyes are stable up to 315 °C, after that they start to decompose with partial oxidation. Major combustion products are SO and SO_2, CO, N_2 and CO_2, although there are also products of non-oxidative decomposition such as $[C_3N]^+$ (50), $[C_4H_2]^+$ (50), $[C_4N]^+$ (62), $[CS_2]^+$ (76), $[C_6H_4]^+$ (76), $[C_6H_6]^+$ (78), $[C_5H_{5–6}]^+$ (65–66) which have been detected by mass spectrometry. Water is also formed although in small amounts, while acetic acid is one of the main decomposition products. Combustion still is not finished at 500 °C (~40% of initial mass).These data show that the thermal stability of the obtained dyes is good enough for applications in DSSCs.

UV-VIS absorption and emission spectra of dyes **4a–e** were recorded in chloroform solution [Figure 2(*a*) and Table 1]. The broad absorption band of these dyes occurs in the visible region at 400–650 nm, which is due to intramolecular charge transfer (πD–π*A) from the donor fragment of thieno[3,2-*b*]indole or benzo[*g*]thieno[3,2-*b*]indole to the acceptor-anchoring part MRAA. Among these dyes, **4e** displays a red-shift maximum absorption wavelength at 535 nm with a molar absorption coefficient of

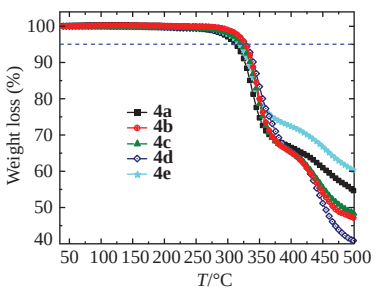


Figure 1 Thermogravimetric analysis of dyes **4a–e**.

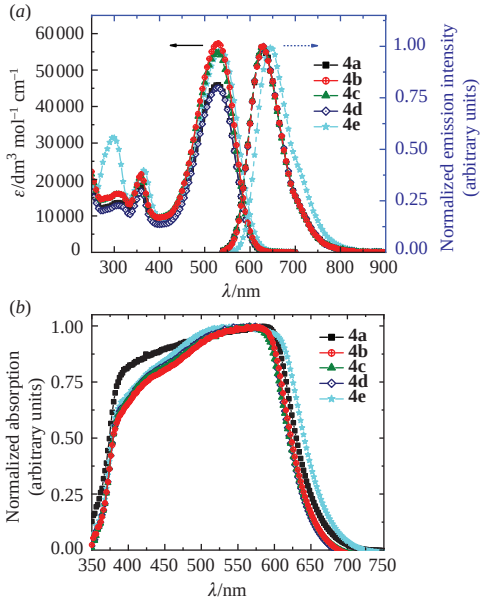


Figure 2 Absorption and emission spectra of dyes **4a–e** (*a*) in $CHCl_3$ and (*b*) on TiO_2 films.

Table 1 Optical and electrochemical data of dyes **4a–e**.

Dye	λ_{max}[a]/ nm	ε[b]/ $dm^3\ mol^{-1}\ cm^{-1}$	λ_{em}[c]/ nm	$E_{0–0}$[d]/ eV	λ_{max}[e]/ nm	E_{ox}^{onset}/ V	E_{HOMO}/ eV	E_{LUMO}[f]/ eV
4a	528	46300	627	2.12	573	0.71	–5.37	–3.25
4b	528	57300	630	2.11	565	–	–	–
4c	528	54800	626	2.11	569	–	–	–
4d	529	45000	630	2.12	566	0.70	–5.36	–3.24
4e	535	56200	644	2.04	543	0.83	–5.49	–3.45

[a] Absorption maximum of the dye in $CHCl_3$ solution. [b] The molar extinction coefficient in $CHCl_3$. [c] Fluorescence emission maximum in $CHCl_3$. [d] The band gap $E_{0–0}$ was derived from the intersecting point of absorption and normalized emission spectra in $CHCl_3$. [e] Absorption maximum of dye adsorbed onto the TiO_2 film. [f] $E_{LUMO} = E_{0–0} + E_{HOMO}$.

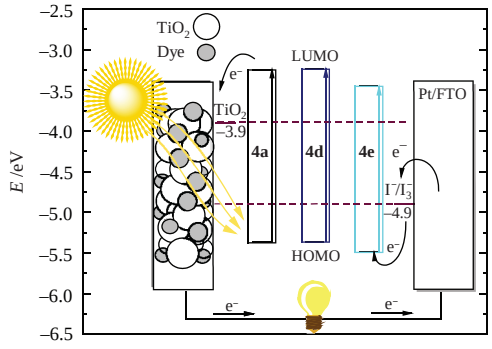


Figure 3 Schematic energy levels for dyes **4a**,**d**,**e**, a nanocrystalline TiO_2 electrode and I_3^-/I^- redox electrolyte.

56200 dm^3 mol^{-1} cm^{-1}.The most plausible explanation for this fact is the increasing overall π-conjugation in molecules of dye **4e** due to the presence of additional benzene ring in the donor fragment. For the same reasons, fluorescence maxima increased from **4a**–**d** to **4e** in a range of 626–644 nm. Upon absorption on the surface of the TiO_2 film [Figure 2(*b*)], compounds **4a**–**e** exhibit a bathochromic shift of 8−45 nm compared with those in solutions, which is attributable to *J*-type dyes aggregation at the TiO_2 film.[26,27] Note that the absorption of **4e** anchored on the surface of the TiO_2 film shows the lower bathochromic shift compared with dyes **4a**–**d**.

To study the electrochemical behavior of synthesized dyes **4a** and **4d**–**e**, we applied cyclic voltammetry (see Figures 3, S1 and Table 1). On the basis of the redox potentials of dyes **4a** and **4d**,**e**, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy values were calculated (see Table 1). In comparison with **4e**, the HOMO of **4a** and **4d** is high-lying (shifted by ~0.13 eV), indicative of an attenuated driving force for the regeneration of the oxidized dye. On the other hand, the LUMO energies of dyes **4a** and **4d**–**e** were more negative to the conduction band energy of TiO_2 (–3.9 eV) pointing out that excited electrons injection into TiO_2 electrode can be spontaneous. In this way, these dyes are appropriate as photosensitizers for DSSCs.

The photovoltaic characteristics of DSSCs based on dyes **4a**–**e** were recorded under simulated solar light AM 1.5 G, 100 mW cm^{-2} (Figure 4 and Table 2). In addition, Ru^{II}-based dye **N3** [*cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) ruthenium(II)] was used as the reference photosensitizer. The DSSC based on **4e** exhibits the best power conversion efficiency (PCE) of 1.09% among the dyes **4a**–**e**, with a short-circuit photocurrent density (J_{sc}) of 3.01 mA cm^{-2},

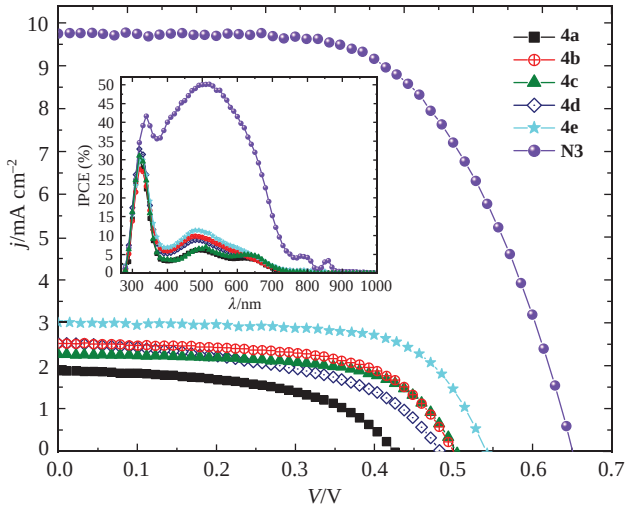


Figure 4 *J*/*V* curves of DSSCs and IPCE (inset) spectra of dyes **4a**–**e** and **N3**.

Table 2 Photovoltaic performance of the fabricated DSSCs based on dyes **4a**–**e** and **N3**.

Dye	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	PCE (%)
4a	1.88	0.42	0.54	0.42
4b	2.52	0.49	0.62	0.77
4c	2.26	0.49	0.64	0.72
4d	2.52	0.48	0.50	0.60
4e	3.01	0.53	0.69	1.09
N3	9.77	0.64	0.61	3.80

an open-circuit photovoltage (V_{oc}) of 0.53 V, and a fill factor (FF) of 0.69, respectively. The higher open-circuit voltages of DSSC based on **4e** can be ascribed to its low-lying HOMO energy level dyes. The incident photon-to-current efficiency (IPCE) measurement showed that dyes **4a**–**e** had low quantum efficiency over the visible region.

In summary, we have synthesized a series of new D–π–A dyes **4a**–**e**, containing thieno[3,2-*b*]indole or benzo[*g*]thieno-[3,2-*b*]indole core as donor parts and 5-(methylene)rhodanine-3-acetic acid as an acceptor part, and used these dyes as photosensitizers for DSSCs. The DSSCs based on dyes **4a**–**e** exhibited values of PCE in the range of 0.42–1.09%.

The synthesis and analytical study of organic materials was performed with the financial support of the Russian Science Foundation (project no. 19-13-00234). The study of dye-sensitized solar cells was carried out with the financial support of the Russian Science Foundation (project no. 18-13-00409).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.07.030.

References

1 S.-H. Nam, K. H. Lee, J.-H. Yu and J.-H. Boo, *Appl. Sci. Convergence Technol.*, 2019, **28**, 194.
2 C.-P. Lee, R. Y.-Y. Lin, L.-Y. Lin, C.-T. Li, T.-C. Chu, S.-S. Sun, J. T. Lin and K.-C. Ho, *RSC Adv.*, 2015, **5**, 23810.
3 C. Dragonetti and A. Colombo, *Molecules*, 2021, **26**, 2461.
4 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
5 M. Grätzel, *J. Photochem. Photobiol., C*, 2003, **4**, 145.
6 A. Mishra, M. K. R. Fischer and P. Bäuerle, *Angew. Chem., Int. Ed.*, 2009, **48**, 2474.
7 S. Chaurasia and J. T. Lin, *Chem. Rec.*, 2016, **16**, 1311.
8 A. E. Egorov, A. A. Kostyukov, I. E. Borissevitch and V. A. Kuzmin, *Mendeleev Commun.*, 2021, **31**, 68.
9 T. N. Murakami and N. Koumura, *Adv. Energy Mater.*, 2019, **9**, 1802967.
10 M. L. Keshtov, S. A. Kuklin, I. O. Konstantinov, Y. Zou and G. D. Sharma, *Mendeleev Commun.*, 2021, **31**, 800.
11 G. M. Ziarani, R. Moradi, N. Lashgari and H. G. Kruger, *Metal-Free Synthetic Organic Dyes*, Amsterdam, Elsevier, 2018.
12 R. A. Irgashev, A. S. Steparuk and G. L. Rusinov, *Org. Biomol. Chem.*, 2018, **16**, 4821.
13 R. A. Irgashev, A. S. Steparuk and G. L. Rusinov, *Tetrahedron Lett.*, 2019, **60**, 151185.
14 A. S. Steparuk, R. A. Irgashev, G. L. Rusinov, E. V. Krivogina, P. I. Lazarenko and S. A. Kozyukhin, *Russ. Chem. Bull.*, 2019, **68**, 1208.
15 L. Zhang and J. M. Cole, *ACS Appl. Mater. Interfaces*, 2015, **7**, 3427.
16 V. V. Dotsenko, D. S. Buryi, D. Yu. Lukina and S. G. Krivokolysko, *Russ. Chem. Bull.*, 2020, **69**, 1829.
17 M. Mao, X.-L. Zhang, X.-Q. Fang, G.-H. Wu, Y. Ding, X.-L. Liu, S.-Y. Dai and Q.-H. Song, *Org. Electron.*, 2014, **15**, 2079.
18 D. D. Babu, S. R. Gachumale, S. Anandan and A. V. Adhikari, *Dyes Pigm.*, 2015, **112**, 183.
19 D. D. Babu, D. Elsherbiny, H. Cheema, A. El-Shafei and A. V. Adhikari, *Dyes Pigm.*, 2016, **132**, 316.
20 S. Fuse, S. Sugiyama, M. M. Maitani, Y. Wada, Y. Ogomi, S. Hayase, R. Katoh, T. Kaiho and T. Takahashi, *Chem. – Eur. J.*, 2014, **20**, 10685.
21 S. S. M. Fernandes, M. C. R. Castro, A. I. Pereira, A. Mendes, C. Serpa, J. Pina, L. L. G. Justino, H. D. Burrows and M. M. M. Raposo, *ACS Omega*, 2017, **2**, 9268.

22 D. S. Patil, K. K. Sonigara, M. M. Jadhav, K. C. Avhad, S. Sharma, S. S. Soni and N. Sekar, *New J. Chem.*, 2018, **42**, 4361.
23 C. A. Echeverry-Gonzalez, A. Ortiz and B. Insuasty, *New J. Chem.*, 2019, **43**, 8781.
24 S. S. M. Fernandes, M. M. M. Raposo, I. Mesquita, L. Andrade, A. Mendes, L. L. G. Justino and H. D. Burrows, *Org. Electron.*, 2017, **49**, 194.
25 M. R. Elmorsy, R. Su, A. A. Fadda, H. A. Etman, E. H. Tawfik and A. El-Shafei, *Dyes Pigm.*, 2018, **158**, 121.
26 K. Avhad, M. Jadhav, D. Patil, T. H. Chowdhury, A. Islam, I. Bedja and N. Sekar, *Org. Electron.*, 2019, **65**, 386.
27 L. Zhang and J. M. Cole, *J. Mater. Chem. A*, 2017, **5**, 19541.

Received: 20th December 2021; Com. 21/6778