Optics and Spectroscopy, 2024, Vol. 132, No. 7

02

Synthesis and study of optical application of organic dyes based on substituted 4-oxo-2-(thiophen-2-yl)aminobut-2-enoic acids

© I.A. Gorbunova[1], D.I. Klimenko[1], M.A. Rider[1], E.S. Denislamova[2], D.A. Shipilovskikh[2,3],
S.A. Cherevkov[1], S.A. Shipilovskikh[1,*]

[1] International research and educational center for physics of nanostructures, ITMO University,
Saint-Petersburg, Russia
[2] Perm Research Polytechnic University,
Perm, Russia
[3] Peter the Great Saint-Petersburg Polytechnic University,
Saint-Petersburg, Russia
e-mail: i_gorbunova@itmo.ru, shipilovskikh@itmo.ru

Received April 27, 2024
Revised July 05, 2024
Accepted July 05, 2024

Highly photoluminescent organic dyes are key materials for organic optoelectronics and photonics. In this paper, we report on the rational design of organic dyes based on substituted 2-(thiophen-2-yl)amino-4-oxobut-2-enoic acids, which are synthesised by a sequential multistep method from substituted 2-hydroxy-4-oxobut-2-enoic acids and the ethyl 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophen-3-carboxylate. The ability of modification of the chemical structure of the dyes during synthesis allows the introduction of different structural fragments that have a significant effect on the optical properties of the target materials. The obtained organic dyes possess effective photoluminescence (PL) in the orange-red region of the spectrum from 596 to 635 nm in powdered form. At the same time, solvents convert them to a non-luminescent state, and a red shift of the main absorption maximum occurs during the transition from nonpolar to polar solvents, which suggests a significant influence of the formed hydrogen bonds inside the molecule during the formation of a rigid crystal structure.

Keywords: organic dyes, photoluminescence, substituted 2,4-dioxobutanoic acids, 2-aminothiophenes.

DOI: 10.61011/EOS.2024.07.59647.6445-24

Introduction

In the modern digital technology world, optical devices and sensors made on their basis play a vital role in photonic production [1,2]. Organic materials with luminescent properties attract the attention of many researchers [3–5] and are used in various applications [6–8], including the development of display units [9,10], lasers [11] and biological visualization technologies [12,13]. These organic materials play an equally important role in the development of dyes and inks for modern anti-counterfeiting technologies [14–16]. The dyes shall meet the specified requirements, including convenient production, low cost, low toxicity for humans and environment. Thus, the problem of creating new materials that meet all applicable requirements is still important.

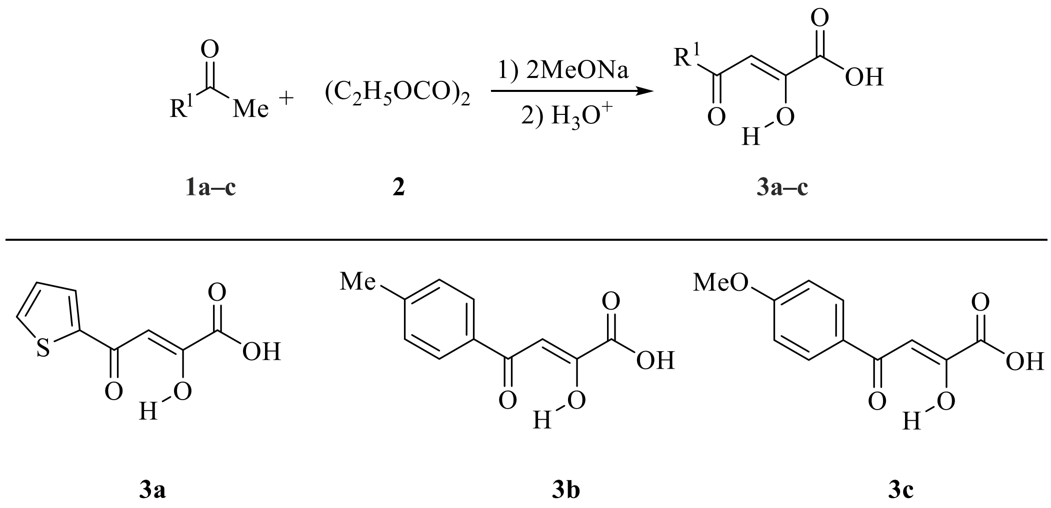
Structures containing several interrelated thiophene rings such as terthiophenes [17], thiophene-vinyl-thiophenes [18], ditienothiophenes [19], etc. [20–22] are currently widely investigated as organic compounds for optical applications. However, 2-aminothiophene derivatives that have a wide range of biological applications [23] are not addressed in the optical application area, whence it follows that this class of compounds may be treated as potential biocompatible optical materials.

We have shown before that structures such as substituted 2-amino-4-oxobut-2-ene acids synthesized on the basis of substituted 2-aminothiophenes had a luminescence capability [24]. Such structures are also applicable to fabrication of thin films on their basis [25] and may be used in biocompatible ink manufacturing for optical visualization [26]. This study continued the investigation of optical properties of this class of compounds, in particular, the effect produced by their chemical structure of organic dyes on their solid-state luminescence was examined and the behavior of dyes in heteropolar organic solvents was investigated.

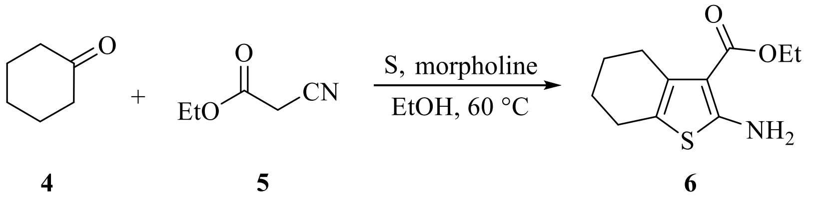
Materials and research methods

Materials

The study used 2-acetylthiophene (98%), 4′-methylacetophenone (95%), 4′-methoxyacetophenone (99%), diethyl oxalate ($\geq$ 99%), sodium methoxide (95%), cyclohexanone ($\leq$ 99.0%), cyan-acetic ester ($\geq$ 98%), sulfur (99.98%), methanol ($\geq$ 99.0%), acetonitrile ($\geq$ 99.0%), ethanol (95%), chloroform-D (99.8 atom% D), dimethylsulfoxide (DMSO, $\geq$ 99.5%), chloroform ($CHCl_3$, $\geq$ 99.5%), and acetone ($\geq$ 99.5%). All chemicals were



Scheme 1. Synthesis of substituted 2-hydroxy-4-oxobut-2-ene acids **3a**–**c** and structures of resultant compounds.



Scheme 2. Synthesis of 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylic ester **6**.

used without additional purification. Before using, methanol, acetonitrile and ethanol were dried over activated carbon molecular sieves (3 Å) during two days.

Equipment and research methods

Melting temperatures were measured using the Stuart SMP40 (UK) instrument. Infrared (IR) spectra were recorded using the FSM-1202 (Russia) instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using the Avance III (operating frequency 400 MHz and 100 MHz; Bruker, Germany) instrument. NMR chemical shifts are given with respect to residual signals of $CHCl_3$ (δ_H 7.27 ppm, δ_C 77.0 ppm). Absorption spectra of the samples were measured using the UV Probe 3600 (Shimadzu, Japan) spectrophotometer. Photoluminescence (PL) spectra were recorded using the LSM-710 (Carl Zeiss, Germany) confocal laser scanning microscope with 405 nm laser excitation. Quantum yield of organic dyes was measured using the RF-6000 (Shimadzu, Kyoto, Japan) spectrofluorometer integrating sphere with 405 nm excitation.

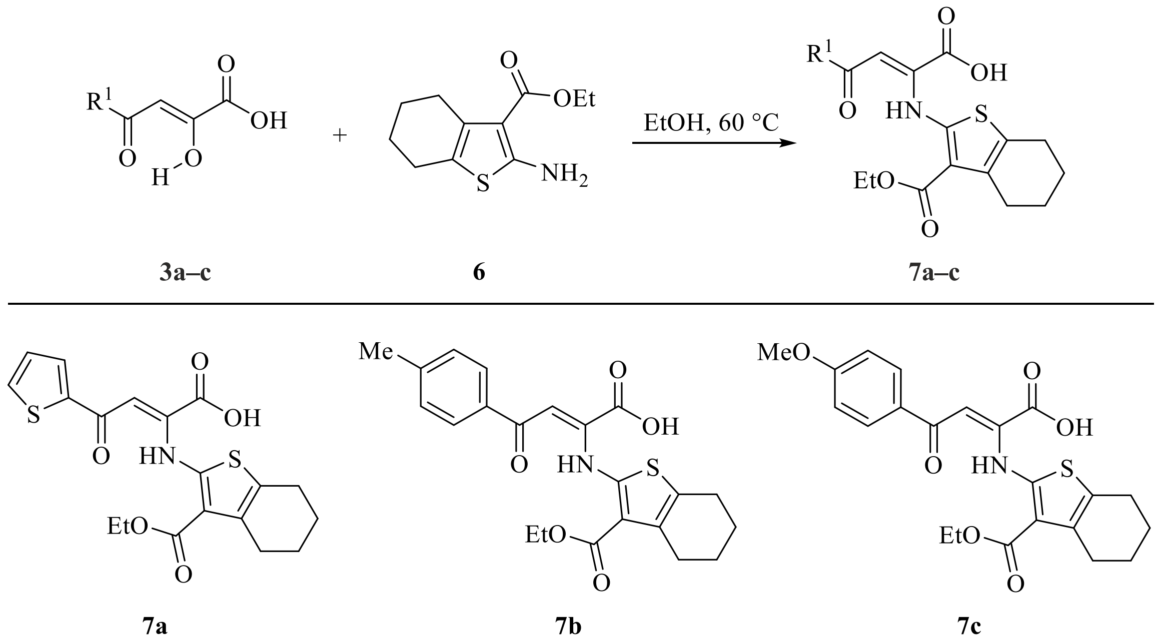
Synthesis of organic dyes based on substituted 2-(thiophen-2-yl)amino-4-oxobut-2-ene acids

For the study of organic dyes, we have chosen a series of substituted 2-(thiophene-2-yl)amino-4-oxobut-2-ene acids synthesized in 3 stages.

Stage 1. *General procedure for the synthesis of substituted 2-hydroxy-4-oxobut-2-ene acids* **3a**–**c**. Sodium methoxide solution (0.2 M) in 50 ml of methanol was slowly added to a mixture (0.1 M) of appropriate ketones **1a**–**c** and (0.1 M) diethyl oxalate **2**. After 24 hours, the precipitate was dissolved in water heated to 60°C and then the solution was acidified with concentrated hydrochloric acid to pH 3. The precipitate was filtered and recrystallized from acetonitrile (Scheme 1).

Stage 2. *Synthesis of 2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylic ester* **6**. Equimolar amounts of (0.1 M) cyclohexanone **4**, cyan-acetic ester **5** and finely ground sulfur in 40 ml of ethanol were placed into a three-neck flask furnished with a reflux condenser, thermometer and drop funnel. To the resulting solution, 4 ml of morpholine was added dropwise while stirring, taking care to avoid overheating of the reaction mixture. Thirty minutes after complete sulfur dissolution, the resulting solution was cooled, the precipitate was filtered and recrystallized from methanol (Scheme 2).

Stage 3. *Synthesis of substituted 2-amino-4-oxobut-2-ene acids* **7a**–**c**. Solution (0.01 M) of 2-amino-4,5,6,7-tetrahydobenzo[*b*]thiopene-3-carboxylic ester **6** in 20 ml of ethanol is added to the solution of appropriate compounds **1a**–**c** (0.01 M) in 20 ml of ethanol. The resulting solution is held at 60°C during 30 min, and then cooled at −18°C. The precipitate was filtered and recrystallized from ethanol



Scheme 3. Synthesis of organic dyes based on substituted 2-(thiophen-2-yl)amino-4-oxobut-2-ene acids **7a–c** and resultant products.

(Scheme 3). Compounds **7a–c** were produced in accordance with the previously described procedure [27].

Characterization of parent compounds 3a–c and 6

2-hyroxy-4-oxo-4-(thiophen-2-yl)but-2-ene acid (3a). Yield is 30.12 g (76%). Yellow crystals. Melting temperature is 171–172°C (170–173°C [28]). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), d, ppm: 7.89 (m, 2H), 7.57 (m, 2H), 6.37 (s, 1H).

2-hyroxy-4-oxo-4-(p-tolyl)but-2-ene acid (3b). Yield 18.15 g (88%). White crystals. Melting temperature is 141–143°C (141–142°C [29]). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), d, ppm: 7.94 (m, 2H), 7.35 (m, 2H), 7.16 (s, 1H), 2.48 (s, 3H).

2-hydroxy-4-(4-methoxyphenyl)-4-oxobut-2-ene acid (3s). Yield is 20.00 g (89%). White crystals. Melting temperature is 160–161°C (162–164°C [30]). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), d, ppm: 8.02 (m, 2H), 7.12 (m, 1H), 7.02 (s, 2H), 3.93 (s, 3H).

2-amino-4,5,6,7-tetrahydrobenzo[b]thiophen-3-carboxylic ester (6). Yield is 19.15 g (85%). Yellow crystals. Melting temperature is 117–118°C (117–119°C [31]). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), d, ppm: 5.93 (s, 2H), 4.28 (q, $J = 7.1$ Hz, 2H), 2.73 (m, 2H), 2.52 (m, 2H), 1.79 (m, 4H), 1.36 (t, $J = 7.1$ Hz, 3H).

Characterization of target organic dyes 7a–c

4-oxo-4-(thiophen-2-yl)-2-((3-(ethoxycarbonyl)-4,5,6,7-tetrahydrobenzol[b]thiophen-2-yl)amino)but-2-ene acid (7a). Yield is 3.60 g (89%). Red crystals. Melting temperature is 157–158°C (158–160°C [32]). Infrared spectrum, ν, cm^{-1}: 1671 br. (COOEt), 3410 (NH). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 12.08 (s, 1H), 7.90 (m, 1H), 7.76 (m, 1H), 7.22 (m, 1H), 7.08 (s, 1H), 4.42 (q, $J = 7.1$ Hz, 2H), 2.85 (m, 2H), 2.78 (m, 2H), 1.85 (m, 4H), 1.42 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 182.1, 164.4, 162.2, 145.4, 144.6, 144.3, 135.7, 134.9, 133.3, 129.2, 129.2, 118.3, 97.1, 61.5, 26.6, 25.0, 23.0, 22.6, 14.4.

4-(4-methylphenyl)-4-oxo-2-((3-(ethoxycarbonyl)-4,5,6,7-tetrahydrobenzol[b]thiophen-2-yl)amino)but-2-ene acid (7b). Yield is 3.96 g (96%). Orange crystals. Melting temperature is 187–189°C (188–189°C [27]). Infrared spectrum, ν, cm^{-1}: 1715 (COOEt), 3442 (NH). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 12.11 (s, 1H), 7.96 (m, 2H), 7.34 (m, 2H), 7.18 (s, 1H), 4.43 (q, $J = 7.1$ Hz, 2H), 2.86 (m, 2H), 2.77 (m, 2H), 2.46 (s, 3H), 1.85 (m, 4H), 1.42 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 189.5, 164.4, 162.5, 146.3, 145.1, 144.4, 135.1, 134.9, 129.9, 129.2, 129.0, 118.4, 96.9, 61.5, 26.6, 25.1, 23.0, 22.6, 21.9, 14.4.

4-(4-methoxyphenyl)-4-oxo-2-((3-(ethoxycarbonyl)-4,5,6,7-tetrahydrobenzol[b]thiophen-2-yl)amino)but-2-ene acid (7c). Yield is 4.03 g (94%). Red crystals. Melting temperature is 187–188°C (186–187°C [33]). Infrared spectrum, ν, cm^{-1}: 1712 (COOEt), 3412 (NH). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 12.07 (s, 1H), 8.04 (m, 2H), 7.11 (m, 1H), 7.00 (s, 2H), 4.40 (q, $J = 7.1$ Hz, 2H), 3.91 (m, 3H), 2.84 (m, 2H), 2.77 (s, 2H), 1.85 (m, 4H), 1.41 (t, $J = 7.1$ Hz, 3H).

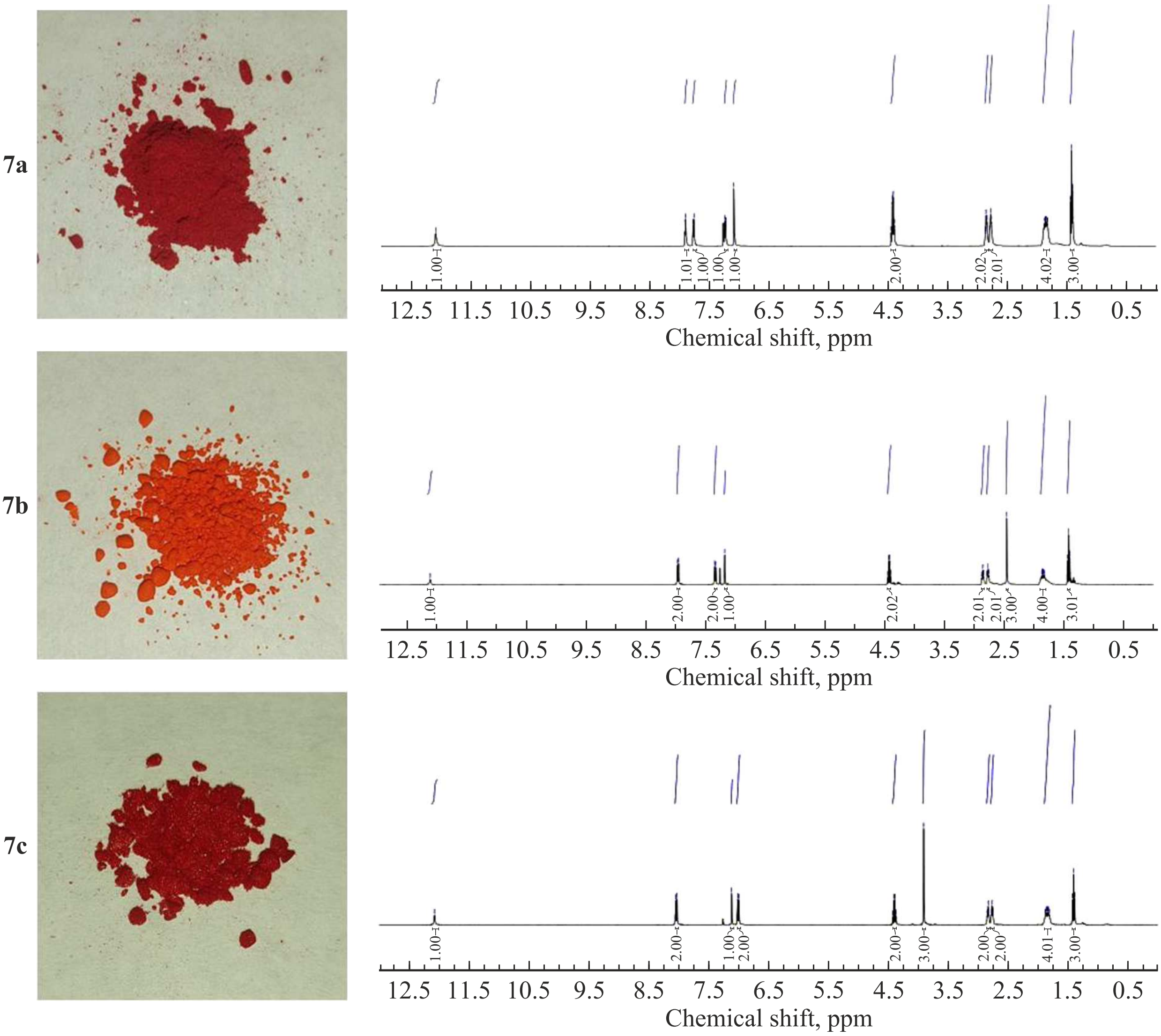


Figure 1. Photographs of powders and ^{1}H NMR spectra of dyes **7a**–**c.**

Findings and discussion

This paper reports the multi-stage synthesis of substituted 2-(thiophen-2-yl)amino-4-oxobut-2-ene acids **7a**–**c** that were used as model organic dyes. For this, parent substituted 2-hydroxy-4-oxobut-2-ene acids **3a**–**c** (Scheme 1) were made at the first stage by interaction between substituted methylketones **1a**–**c** and diethyl oxalate **2** in the presence of two sodium methoxide equivalents in methanol followed by intermediate salt decomposition.

Then, the Gewald reaction one-pot technique was used to synthesize 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylic ester **6** (Scheme 2) by interaction between cyclohexanone **4** and cyan-acetic ester.

Further interaction between substituted 2-hydroxy-4-oxobut-2-ene acids **3a**–**c** and 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylic ester **6** gave the studied organic dyes based on substituted 2-(thiophen-2-yl)amino-4-oxobut-2-ene acids **7a**–**c** (Scheme 3).

The structure of the resultant compounds was confirmed by the IR and NMR spectroscopy methods. Compounds **7a**–**c** — red crystalline substances produced with chemical yields of 89–96% are highly soluble in DMSO, chloroform, when heated in toluene, acetonitrile and alcohols, however, insoluble in water and alkanes. According to the ^{1}H NMR spectra in $CDCl_3$, compounds **7a**–**c** are characterized by the presence of the NH-group singlet proton at 12.07–12.11 ppm and by the CH-group singlet proton at 7.08–7.18 ppm (Figure 1).

Then, the optical properties of the resultant organic dyes were studied **7a**–**c.** Absorption spectra of dye solutions in organic solvents (acetone, dimethylsulfoxide, chloroform) (Figure 2), solid-state luminescences (Figure 3) and quantum yields of the resultant dyes were measured. Quantum yields of the resultant organic dyes measured

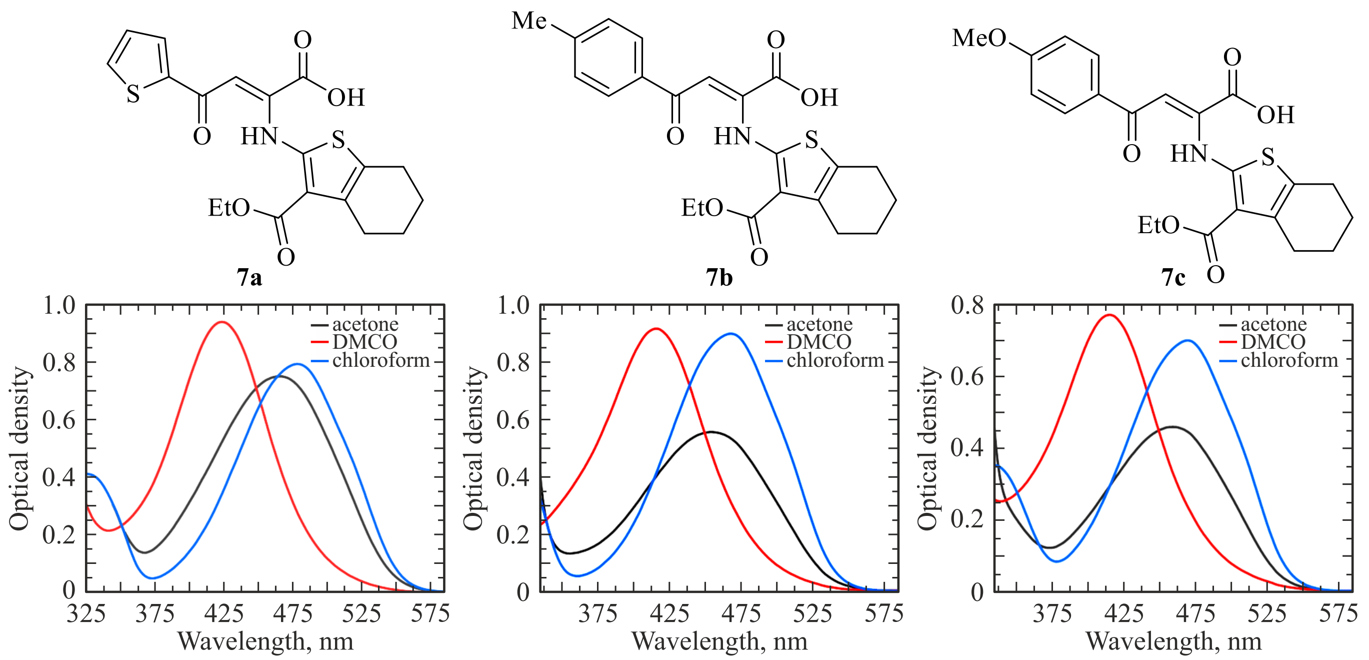


Figure 2. absorption spectra of organic dye **7a–c** solutions in acetone, DMSO and chloroform.

for the crystalline form using the spectrofluorophotometer integrating sphere with 405 nm excitation are equal to 14.4% for compound **7a**, 26.3% for compound **7b** and 16.1% for compound **7c.**

When recording the absorption spectra, concentration o the studied organic dyes for each of the sample measurement series in various solvents was the same and equal to 7 μg/ml for dye **7a**, 20 μg/ml or dye **7b,** 17 μg/ml for dye **7c.** Figure 2 shows that, when using acetone, the absorption band peaks for dyes **7a**, **7b** and **7c** were at 464 nm, 455 nm and 460 nm, respectively For dye **7a–c** solutions in chloroform, there was a minor red shift of the absorption bands with respect to those of the solution in acetone. The red shift was 15 nm, 13 nm and 10 nm for dyes **7a**, **7b**, **7c**, respectively. For dye **7a–c** solutions in DMSO, absorption bands are shifted to the short-wavelength domain (at 41 nm for **7a,** at 39 nm for **7b,** at 45 nm for **7c**).

Note also that the optical density at the absorption band peak for dye **7a–c** solutions in acetone turned to be lower than that of the solutions in DMSO and chloroform. As the solvent polarity increases, blue shift of the absorption band is observed, which is confirmed by the obtained spectral data. Thus, variations in the absorption band positions and intensities are observed due to transformations induced by the interaction between the solvent molecules and the substance. This fact suggests formation of hydrogen bonds within the molecule, which agrees with the NMR spectra.

When comparing the PL spectra of the dyes measured throughout the examined area of dyes **7a–c**,, it can be seen that the PL bands for all compounds are broadened, full widths at half maximum for dyes **7a**, **7b** and **7c** are 74 nm, 67 nm and 89 nm, respectively. The PL bands for dyes **7a** and **7c** have almost identical position with the luminescence peak at about 635 nm, while the PL band for dye **7b** is shifted to the short-wavelength domain with the luminescence peak at 596 nm (Figure 3).

By the luminescent image of dye **7c**, two types of structures were identified — bars and dot aggregates having apparently different quantum yields. However, the PL band of dots has a minor blue shift of 26 nm with respect to the PL band of bars (Figure 4).

Conclusion

Thus, this study demonstrated an approach to streamlined design of luminescent fine organic dyes. This approach was used to create a number of organic dyes on the basis of substituted 2-(thiophen-2-yl)amino-4-oxobut-2-ene acids by varying substituents in the final dye structure. The developed procedure was used to achieve significant increase in the quantum yield and stability of dyes, which supports our original hypothesis. Moreover, chemical structure adjustability of dyes during synthesis makes it possible to introduce various structural components that have a significant effect on the optical properties of target materials. The studies demonstrated correlation between the resultant materials and identified optical effect.

Thus, it was shown that the resultant organic dyes have effective PL in the orange-red spectrum range from 596 nm to 635 nm in the powder form. It was found that solid-state

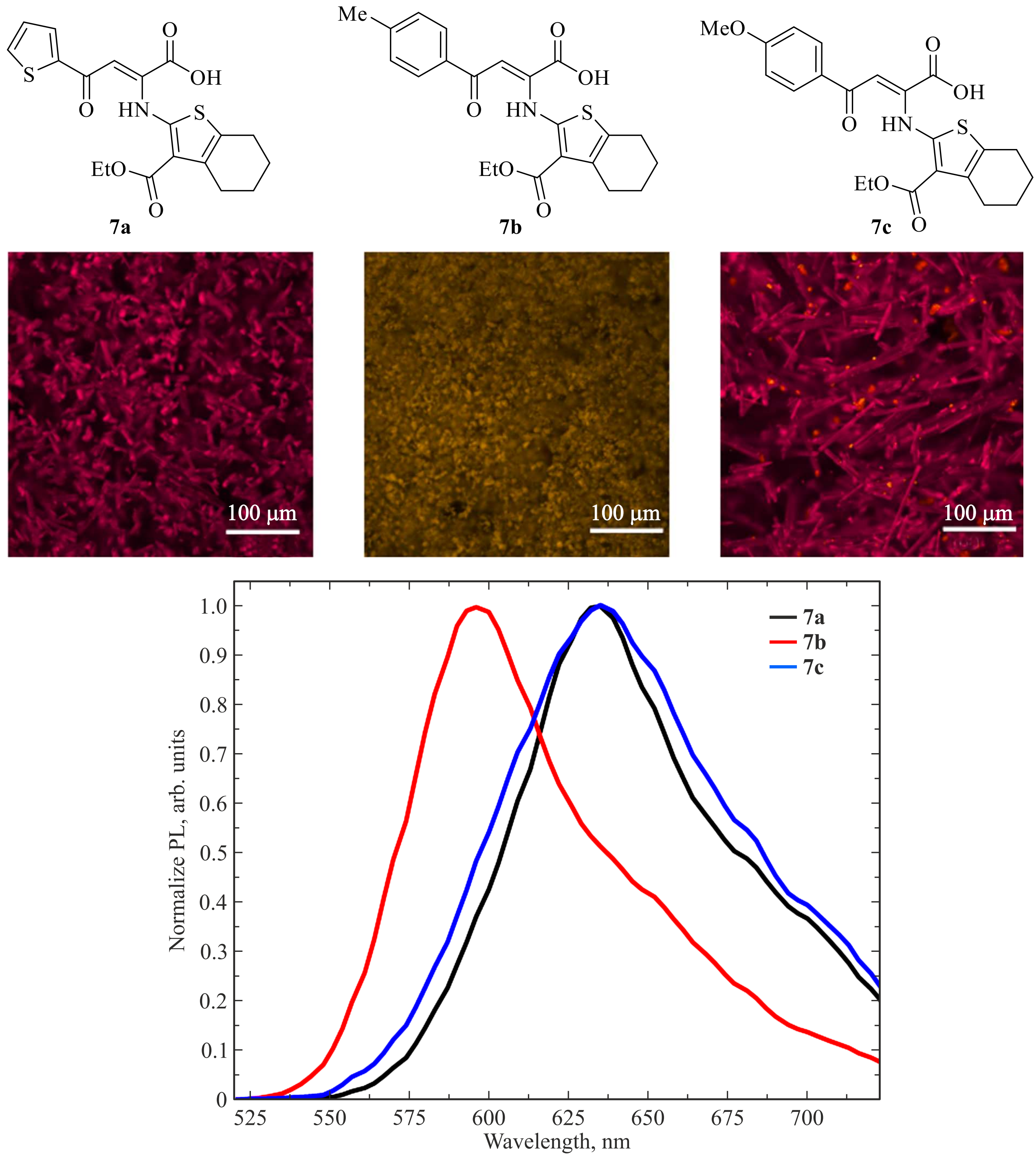


Figure 3. Luminescent images and normalized PL spectra of dyes **7a**–**c**.

luminescence of the resultant dyes is much more effective than in acetone, dimethylsulfoxide and chloroform solutions. While for traditional luminescent materials, luminescence gets dozens or even hundreds of times weaker in going from solutions to solid materials, which renders their further use in modern devices impossible. The described advantages of the materials based on organic dyes with effective PL produced in the study make it possible to offer them as solid-state components of organic optoelectronic devices.

Funding

This study was carried out under the financial support provided by the Russian Science Foundation (grant №. 22-73-10069).

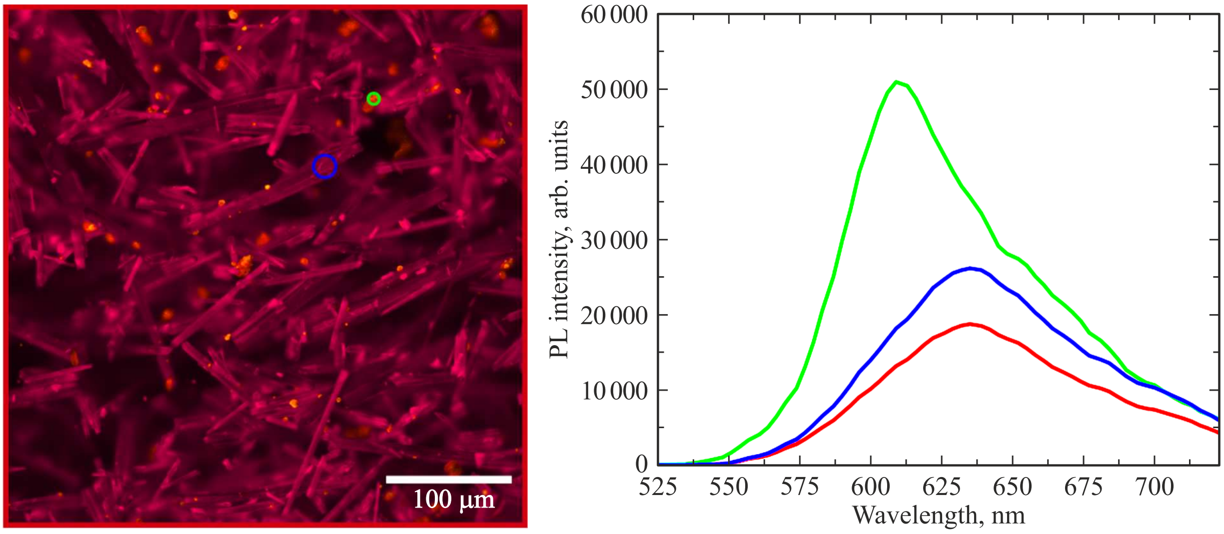


Figure 4. Luminescent image of dye **7c** and non-normalized PL spectra recorded in various segments of the sample; PL spectra demonstrate a signal recorded in the marked segments on the luminescent image, colors of the marked segments correspond to the color of the curve.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] N.L. Kazanskiy, S.N. Khonina, M.A. Butt, A. Kaźmierczak, R. Piramidowicz. Electronics, **10** (8), 973 (2021). DOI: 10.3390/electronics10080973

[2] M.A. Butt, S.N. Khonina, N.L. Kazanskiy. Opt. Laser Technol., **142**, 107265 (2021). DOI: 10.1016/j.optlastec.2021.107265

[3] K. Jinnai, R. Kabe, Z. Lin, C. Adachi. Nat. Mater., **21**, 338 (2022). DOI: 10.1038/s41563-021-01150-9

[4] M. Shimizu, T. Hiyama. Chem. Asian J., **5** (7), 1516 (2010). DOI: 10.1002/asia.200900727

[5] J. Gierschner, J. Shi, B. Milián-Medina, D. Roca-Sanjuán, S. Varghese, S.Y. Park. Adv. Opt. Mater., **9** (13), 2002251 (2021). DOI: 10.1002/adom.202002251

[6] N.A. Kukhta, M.R. Bryce. Mater. Horizons, **8** (1), 33 (2021). DOI: 10.1039/D0MH01316A

[7] J. Han, S. Guo, H. Lu, S. Liu, Q. Zhao, W. Huang. Adv. Opt. Mater., **6** (17), 1800538 (2018). DOI: 10.1002/adom.201800538

[8] X. Feng, X. Wang, C. Redshaw, B.Z. Tang. Chem. Soc. Rev., **52** (19), 6715 (2023). DOI: 10.1039/D3CS00251A

[9] W. Chen, F. Song. Chin. Chem. Lett., **30** (10), 1717 (2019). DOI: 10.1016/j.cclet.2019.08.032

[10] Y. Zhang, J. Song, J. Qu, P.C. Qian, W.Y. Wong. Sci. China Chem., **64**, 341 (2021). DOI: 10.1007/s11426-020-9901-4

[11] Y. Jiang, Y.Y. Liu, X. Liu, H. Lin, K. Gao, W.Y. Lai, W. Huang. Chem. Soc. Rev., **49** (16), 5885 (2020). DOI: 10.1039/D0CS00037J

[12] W. Cheng, H. Chen, C. Liu, C. Ji, G. Ma, M. Yin. View, **1** (4), 20200055 (2020). DOI: 10.1002/VIW.20200055

[13] Z. Xing, W. Wu, Y. Miao, Y. Tang, Y. Zhou, L. Zheng, Y. Fu, Z. Song, Y. Peng. Org. Chem. Front., **8** (8), 1867 (2021). DOI: 10.1039/D0QO01425G

[14] P. Kumar, S. Singh, B.K. Gupta. Nanoscale, **8** (30), 14297 (2016). DOI: 10.1039/C5NR06965C

[15] R.S. Bhagya, K. Muthamma, D. Sunil, P. Shetty, S.D. Kulkarni. Chemical Papers, **77** (9), 4905 (2023). DOI: 10.1007/s11696-023-02827-y

[16] R.K. Jain, K. Muthamma, D. Sunil, S.D. Kulkarni, P.J. Anand, N. Dey. Chemical Papers, **77** (11), 6557 (2023). DOI: 10.1007/s11696-023-02958-2

[17] L. Vallan, E. Istif, I.J. Gómez, N. Alegret, D. Mantione. Polymers, **13** (12), 1977 (2021). DOI: 10.3390/polym13121977

[18] Z. Wang, P. Lei, C. Dong, P. Cong, Y. Geng, Y. Chen, Q. Zeng, A. Tang, E. Zhou. J. Mat. Chem. A, **11** (27), 14539 (2023). DOI: 10.1039/D3TA01651J

[19] R. Ali, R. Siddiqui. RSC Adv., **12**, 36073 (2022). DOI: 10.1039/D2RA05768A

[20] I.E. Palamá, G. Maiorano, G. Barbarella, G. Gigli. Nano Select, **4** (8), 463 (2023). DOI: 10.1002/nano.202300007

[21] A. Mori. Bull. Chem. Soc. Jpn., **93** (10), 1200 (2020). DOI: 10.1246/bcsj.20200169

[22] R.S. Fernandes, N.S. Shetty, P. Mahesha, S.L. Gaonkar. J. Fluoresc., **32**, 19 (2022). DOI: 10.1007/s10895-021-02833-x

[23] V. Duvauchelle, P. Meffre, Z. Benfodda. Eur. J. Med. Chem., **238**, 114502 (2022). DOI: 10.1016/j.ejmech.2022.114502

[24] E. Gunina, N. Zhestkij, S. Bachinin, S.P. Fisenko, D.A. Shipilovskikh, V.A. Milichko, S.A. Shipilovskikh. Photonics Nanostruct., **48**, 100990 (2022). DOI: 10.1016/j.photonics.2021.100990

[25] E. Gunina, M. Timofeeva, Yu.A. Kenzhebayeva, S. Bachinin, I.A. Gorbunova, D.A. Shipilovskikh, V.A. Milichko, S.A. Shipilovskikh. Photonics Nanostruct., **56**, 101168 (2023). DOI: 10.1016/j.photonics.2023.101168

[26] E.V. Gunina, I. Gorbunova, S. Rzhevskiy, Yu. Kenzhebayeva, S. Bachinin, D. Shipilovskikh, K. Mitusova, A. Rogova, A.N. Kulakova, A.S. Timin, S. Shipilovskikh, V.A. Milichko. ACS Appl. Opt. Mater., **1** (12), 2013 (2023). DOI: 10.1021/acsaom.3c00340

[27] S.A. Shipilovskikh, R.R. Makhmudov, D.Yu. Lupach, P.T. Pavlov, E.V. Babushkina, A.E. Rubtsov. Pharm. Chem. J., **47** (7), 366 (2013). DOI: 10.1007/s11094-013-0960-z.

[28] A. Bhatt, K.R. Gurukumar, A. Basu, M.R. Patel, N. Kaushik-Basu, T.T. Talele. Eur. J. Med. Chem., **46** (10), 5138 (2011). DOI: 10.1016/j.ejmech.2011.08.028

[29] O.A. Sof'ina, N.M. Igidov, E.N. Koz'minykh, N.N. Trapeznikova, Y.S. Kasatkina, V.O. Koz'minykh. Russ. J. Org. Chem., **37** (7), 1017 (2001). DOI: 10.1023/A:1012438902959

[30] V. Zikán, M. Semonský, B. Kakáč, J. Holubek, K. Řežábek. Collect. Czech. Chem. Commun., **42** (5), 1562 (1977). DOI: 10.1135/cccc19771562

[31] D.A. Ibrahim, J. Boucau, D.H. Lajiness, S.K. Veleti, K.R. Trabbic, S.S. Adams, D.R. Ronning, S.J. Sucheck. Bioconjugate Chem., **23** (12), 2403 (2012). DOI: 10.1021/bc3004342

[32] A. Rogova, I.A. Gorbunova, T.E. Karpov, R.Yu. Sidorov, A.E. Rubtsov, D.A. Shipilovskikh, A.R. Muslimov, M.V. Zyuzin, A.S. Timin, S.A. Shipilovskikh. Eur. J. Med. Chem., **254**, 115325 (2023). DOI: 10.1016/j.ejmech.2023.115325

[33] Yu. Kenzhebayeva, I. Gorbunova, A. Dolgopolov, M.V. Dmitriev, T.S. Atabaev, E.A. Stepanidenko, A.S. Efimova, A.S. Novikov, S. Shipilovskikh, V.A. Milichko. Adv. Photonics Res., **5** (2), 2300173 (2024). DOI: 10.1002/adpr.202300173

Translated by E.Ilinskaya