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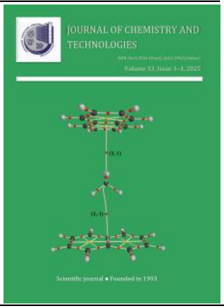

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NEW HYBRID XANTHENE-PYRYLIUM DYES: SYNTHESIS AND SPECTRAL PROPERTIES

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Abstract

In this work we studied the interaction of N'-(4-formyl-2,3-dihydro-1H-xanthen-9-yl)-N,N-dimethylimidoformamide with 2,6-di-tert-butyl-4-methylpyrylium perchlorate and 2-methyl-4,6-diphenylpyrylium tetrafluoroborate in acetic anhydride under various conditions. Thus, when carrying out the reaction with 2,6-di-tert-butyl-4-methylpyrylium perchlorate at 100 °C for 6 h, the corresponding dye is formed with the amidine group replaced by acetyl. In the case of carrying out the reaction with 2-methyl-4,6-diphenylpyrylium tetrafluoroborate at room temperature for 1 h, the dye is formed with the amidine fragment preserved. The absorption spectra of the obtained dyes were recorded in various solvents and the extinction coefficients were calculated. The absorption maximum of 4-{(*E*)-2-[9-(acetylamino)-2,3-dihydro-1*H*-xanthen-4-yl]vinyl}-2,6-di-*tert*-butylpyrylium perchlorate in toluene and chloroform is approximately 675 nm, whereas in water it is hypsochromically shifted to 605 nm. The absorption coefficient of this dye in chloroform is observed to be the highest, with a value that is 5-7 times higher than that in water or toluene. A modification in the polarity of the solvent exerts minimal influence on the absorption maximum of 2-[(*E*)-2-(9-{[(1*E*)-(dimethylamino)methylene]amino}-2,3-dihydro-1*H*-xanthen-4-yl)vinyl]-4,6-diphenylpyrylium tetrafluoroborate, which is situated at approximately 715 nm.

Keywords: xanthene dyes; amidine fragment; absorption spectra; condensation; pyrylium salt.

НОВІ ГІБРИДНІ КСАНТЕН-ПІРИЛІЄВІ БАРВНИКИ: СИНТЕЗ ТА СПЕКТРАЛЬНІ ВЛАСТИВОСТІ

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Анотація

У цій роботі ми досліджували взаємодію N'-(4-форміл-2,3-дигідро-1H-ксантен-9-іл)-N,N-диметилімідоформаміду з перхлоратом 2,6-ди-трет-бутил-4-метилпірилію та тетрафторборатом 2-метил-4,6-дифенілпірилію в оцтовому ангідриді за різних умов. Так, при проведенні реакції з перхлоратом 2,6-ди-трет-бутил-4-метилпірилію при 100 °С протягом 6 годин утворюється відповідний барвник із заміщенням амідинової групи на ацетилильний фрагмент. У випадку проведення реакції з тетрафторборатом 2-метил-4,6-дифенілпірилію при кімнатній температурі протягом 1 години барвник утворюється зі збереженням амідинового фрагмента. Спектри поглинання отриманих барвників були записані в різних розчинниках та розраховані коефіцієнти екстинкції. Максимум поглинання перхлорату 4-{(E)-2-[9-(ацетиламіно)-2,3-дигідро-1H-ксантен-4-іл]вініл}-2,6-ди-трет-бутилпірилія в толуолі та хлороформі становить приблизно 675 нм, тоді як у воді він гіпсохромно зміщений до 605 нм. Найвищий коефіцієнт поглинання цього барвника спостерігається у хлороформі, який у 5-7 разів вище ніж у воді або толуолі. Зміна полярності розчинника має мінімальний вплив на максимум поглинання тетрафторборату 2-[(E)-2-(9-{[(1E)-(диметиламіно)метилен]аміно}-2,3-дигідро-1H-ксантен-4-іл)вініл]-4,6-дифенілпірилія, який розташований приблизно при 715 нм.

Ключові слова: ксантенові барвники; амідиновий фрагмент; спектри поглинання; конденсація; пірилієва сіль.

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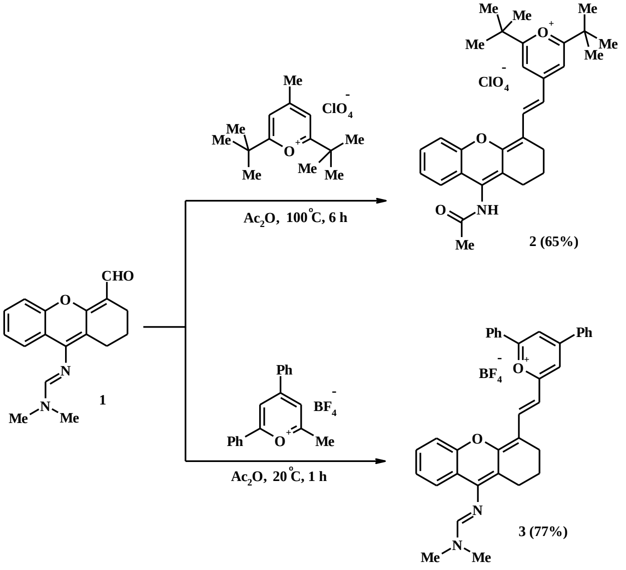
Introduction

The significance of xanthene dyes for contemporary science is challenging to exaggerate [1–6]. These materials have found widespread application in diverse scientific and technological domains [for example, 7–15]. In a previous study, a set of methods for synthesizing the xanthene skeleton was proposed. These methods involved the rearrangement of benzoxazine and benzodioxine derivatives under Vilsmeier-Haack reaction conditions [16–18]. The resulting xanthene derivatives have been shown to be highly versatile building blocks for the synthesis of dyes across a range of colours and with different degrees of fluorescence across the visible spectrum [19–21]. In the present article, a highly convenient synthesis of hybrid xanthene-pyrylium dyes is presented, in addition to a study of some of the optical properties of the new dyes.

Results and Discussion

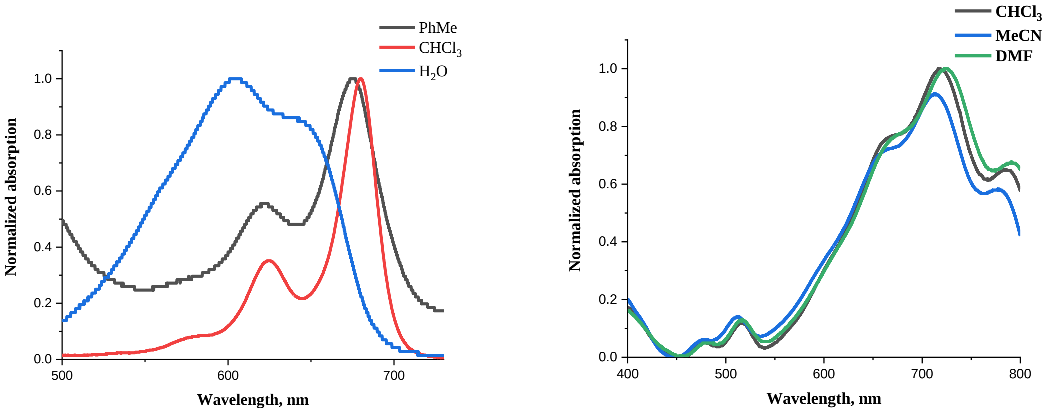
The reaction of aldehyde **1** with various pyrylium salts in acetic anhydride, depending on the reaction conditions, leads to the synthesis of various hybrid xanthene-pyrylium dyes (Scheme). Thus, when carrying out the reaction with 2,6-di-tert-butyl-4-methylpyrylium perchlorate at 100 °C for 6 hours, dye **2** is formed, and with 2-methyl-4,6-diphenylpyrylium tetrafluoroborate at room temperature for 1 hour, dye **3** is formed.



Scheme. Synthesis of dyes 2 and 3

The structure of the synthesized dyes was confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry data. The formation of a new double bond in the *E*-configuration is indicated by the coupling constant between the protons of this bond, which are 14.7 Hz and 14.2 Hz for dyes **2** and **3**, respectively. It is noteworthy that when the reaction is carried out at room temperature, the amidine fragment is retained in the structure of dye **3**, and at elevated temperatures, the amidine fragment is replaced by acetyl (dye **2**).

For the obtained dyes, the absorption spectra were recorded in various solvents, and the extinction coefficients were calculated (Figure and Table).



a **b**

Figure. Absorption spectra of dyes 2 (a) and 3 (b)

The absorption spectra of dyes **2** and **3** were recorded in three solvents of different polarity (Table 1). The absorption maximum of dye **2** in toluene and chloroform is approximately 675 nm, whereas in water it is hypsochromically shifted to 605 nm. The absorption coefficient of this dye in chloroform is observed to be the highest, with a value that is 5–7 times higher than that in water or toluene. The lowest value of the HOMO-LUMO transition energy is observed in toluene. It is important to note that dye **2** is unstable in solution when exposed to water and alcohol, undergoing a chemical transformation within **2** days and acquiring an absorption maximum at 460 nm. A modification in the polarity of the solvent exerts minimal influence on the absorption maximum of dye **3**, which is situated at approximately 715 nm (Table). It has been established that dye **3** exhibits a longer-wave absorption maximum in comparison to dye **2**.

This phenomenon can be attributed to the presence of an electron-donor amidine group within the structure of dye **3**.

Table

The spectral properties[a] of dyes 2 and 3

Solvent	Solvent polarity E_T^N[b]	Compound	λ_{max} (Abs), nm	ε, $M^{-1}\cdot cm^{-1}$	λ_{onset} (Abs)[c], nm	E_g^{opt}[d], eV
PhMe	0.099	2	675	11600	721	1.72
$CHCl_3$	0.259		680	78800	705	1.76
H_2O	1.000		605	14400	670	1.85
$CHCl_3$	0.259	3	718	71800	-	-
DMF	0.386		724	48400	-	-
MeCN	0.460		713	53000	-	-

[a] Absorption ($\lambda_{Abs\text{-}max}$) maxima and extinction coefficients (ε_{max}) were determined experimentally

[b] The normalized values of solvent polarity were taken from [22, 23]

[c] Red limit of intrinsic absorption

[d] E_g^{opt} is the optical energy gap of the HOMO-LUMO transition calculated on the basis of the wavelength of the red limit of intrinsic absorption [24, 25]

Experimental part

Unless otherwise stated, all reagents of analytical grade were purchased from commercial suppliers and used without any further purification. The ^1H and ^{13}C NMR spectra were performed on a Bruker Avance II 400 spectrometer (and 100.62 MHz for ^1H and ^{13}C, respectively) in $CDCl_3$ and DMSO-d_6 using residual solvent peak as an internal standard. The FAB mass spectra of compounds were recorded on a VG7070 spectrometer. Desorption of the ions from the solution of the samples in 3-nitrobenzyl alcohol was realized with a beam of argon atoms with energy 8 keV. Melting points were carried out using an Electrothermal 9100 Digital Melting Point apparatus and were uncorrected. The control of reactions and the purity of the obtained compounds were monitored by TLC on Merck Silica gel 60 F-254 plates with 10 : 1, v/v $CHCl_3$/MeOH as eluent. Absorption spectra were recorded in 1-cm quartz cells at 25 °C using UV-2401 PC spectrophotometer (Shimadzu, Japan).

*4-{(E)-2-[9-(Acetylamino)-2,3-dihydro-1H-xanthen-4-yl]vinyl}-2,6-di-tert-butylpyry-lium perchlorate (**2**).* The 2,6-di-*tert*-butyl-4-methylpyrylium perchlorate 0.54 g (1.77 mmol, 0.54 g) was dissolved in acetic anhydride (5 mL). To the resulting solution, aldehyde 1 (1.77 mmol, 0.5 g) was added and stirred at 100 °C for 6 h. The solvent was then evaporated using a rotary evaporator, and the residue was purified by column chromatography on silica using $CHCl_3$ as the eluent. Yield 0.64 g (65 %), dark blue powder, mp 250–253 °C. ^1H NMR, δ, ppm (DMSO-d_6): 10.23 (1H, br s, NH); 8.75 (1H, d, $^3J=14.7$ *Hz*, CH); 7.66–7.68 (3H, m, H Ar); 7.57 (2H, br s, 2CH pyr.); 7.38 (1H, t, $^3J=7.3$, H Ar); 6.69 (1H, d, $^3J=14.7$ *Hz*, CH); 2.58–2.61 (2H, m, CH_2); 2.48 (2H, m, CH_2 (overlaps with DMSO signal)); 2.20 (3H, s, Me); 1.75–1.78 (2H, m, CH_2); 1.39 (18H, s, 2 t-Bu). ^1H NMR, δ, ppm ($CDCl_3$): 9.31 (1H, br s, NH); 8.48 (1H, d, $^3J=14.2$ *Hz*, CH); 7.81 (1H, d, $^3J=8.1$ *Hz*, H Ar); 7.52 (1H, t, $^3J=7.6$ *Hz*, H Ar); 7.43 (1H, d, $^3J=8.1$ *Hz*, H Ar); 7.33 (1H, t, $^3J=7.6$ *Hz*, H Ar); 6.92 (2H, br s, 2CH pyr.); 6.26 (1H, d, $^3J=14.2$ *Hz*, CH); 2.67–2.70 (2H, m, CH_2); 2.56–2.59 (2H, m, CH_2); 2.41 (3H, s, Me); 1.79–1.81 (2H, m, CH_2); 1.42 (18H, s, 2 t-Bu). ^{13}C NMR, δ, ppm ($CDCl_3$): 185.2; 175.9; 170.1; 164.6, 156.0, 153.2, 143.3, 142.3, 136.2; 132.8; 126.1, 125.4, 120.0; 117.9; 116.3; 115.1; 37.3; 28.0; 26.0; 24.4; 23.6; 19.9. Mass spectrum (FAB), m/z (I_{rel}, %): 458 $[M]^+$ (100).

2-[(*E*)-2-(9-{[(1*E*)-(Dimethylamino)methylene]amino}-2,3-dihydro-1*H*-xanthen-4-yl)vinyl]-4,6-diphenylpyrylium tetrafluoroborate (3). The 2-methyl-4,6-diphenylpyrylium tetrafluoroborate (1.77 mmol, 0.57 g) was dissolved in acetic anhydride (10 mL). To the resulting solution, aldehyde 1 (1.77 mmol, 0.5 g) was added and stirred at 20 °C for 1 h. The solvent was then evaporated using a rotary evaporator, and the residue was purified by recrystallization from MeCN. Yield 0.81 g (77 %), dark blue powder, mp 165–167 °C. ^{1}H NMR, δ, ppm ($CDCl_3$): 8.41 (1H, s, CH); 8.33 (1H, d, *^3J=14.2 Hz*, CH); 8.00–8.03 (2H, m, H Ar); 7.90–7.93 (2H, m, H Ar); 7.65–7.75 (3H, m, H Ar); 7.45–7.63 (7H, m, H Ar); 6.90 (2H, m, CH pyr.); 6.87 (1H, d, *^3J=14.2 Hz*, CH); 3.42 (3H, s, Me); 3.26 (3H, s, Me); 2.85–2.88 (2H, m, CH_2); 2.69–2.72 (2H, m, CH_2); 1.88–1.92 (2H, m, CH_2). Mass spectrum (FAB), m/z (I_{rel}, %): 511 $[M]^+$ (100).

Conclusion

Thus, two new hybrid xanthene-pyrylium dyes were synthesized: 4-{(*E*)-2-[9-(acetylamino)-2,3-dihydro-1H-xanthen-4-yl]vinyl}-2,6-di-tert-butylpyrylium perchlorate (2) and 2-[(*E*)-2-(9-{[(1*E*)-(dimethylamino)methylene]amino}-2,3-dihydro-1H-xanthen-4-yl)vinyl]-4,6-diphenylpyrylium tetrafluoroborate (3). In the first case, due to the reaction in acetic anhydride at 100 °C for 6 hours, a dye with a replacement of the amidine fragment with acetyl is formed, and in the second case, the reaction temperature is lowered to room temperature, which leads to the preservation of the amidine group. Dye 3 has an absorption maximum of ~715 nm in different solvents, and dye 2 has an absorption maximum of approximately 675 nm.

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References

[1] Schramm, S., Weiß, D. (2019). Chapter Two - Fluorescent heterocycles: Recent trends and new developments. *Advances in Heterocyclic Chemistry*, *128*, 103–179. https://doi.org/10.1016/bs.aihch.2018.10.003

[2] Santos, C.M.M., Silva, A.M.S. (2016). Chapter 6.4 - Six-Membered Ring Systems: With O and/or S Atoms. *Progress in Heterocyclic Chemistry*, *28*, 523–578. https://doi.org/10.1016/B978-0-08-100755-6.00015-6

[3] Tahir, H., Saad, M. (2021). Chapter 3 - Using dyes to evaluate the photocatalytic activity. *Interface Science and Technology*, *32*, 125–224. https://doi.org/10.1016/B978-0-12-818806-4.00005-X

[4] Karaman, O., Alkan, G.A., Kizilenis C., Akgul, C.C., Gunbas, G. (2023). Xanthene dyes for cancer imaging and treatment: a material odyssey. *Coordination Chemistry Reviews*, *475*, 214841. https://doi.org/10.1016/j.ccr.2022.214841

[5] Tang, N., Kangshuo, X., Ruian, S., Ding, H., Zeng, Y., J., Y., Fan, C., Liu, G., Pu, S. (2024). A turn-off xanthene-based fluorescent probe for detection of cysteine and its practical application in bioimaging and food samples. *Analytica Chimica Acta*, 1329, 343193. https://doi.org/10.1016/j.aca.2024.343193

[6] Prabakaran, K.O.H., Manivannan R., Park, S.H., Son, Y.-A. (2022). A novel class of xanthene dyes with chemically linked UV absorber molecule and their photophysical properties. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *279*, 121437. https://doi.org/10.1016/j.saa.2022.121437

[7] Wu, Y., Lun, W., Zeng, H., Guo, X., Yang, M., Lan, Q. (2024). A facile near-infrared xanthene fluorescence probe for visualizing of hypochlorous acid in vitro and in vivo. *Analytica Chimica Acta*, *1294*, 342292. https://doi.org/10.1016/j.aca.2024.342292

[8] Zhang, Y., Liu, J., Xiao, J., Li, F., Liu, K., Yang, M., Liu, J. (2025). A PET based colorimetric/fluorescent dual-signal probe for selective detection of hypochlorite in real water samples. *Journal of Molecular Structure*, *1322*, 140568. https://doi.org/10.1016/j.molstruc.2024.140568

[9] Zhang, C.-L., Liu, C., Nie, S.-R., Zhang, Y., Guo, J.-H., Liu, C. (2024). A novel near-infrared fluorescence probe for detecting N_2H_4 and its application in natural environment and biological system. *Dyes and Pigments*, *224*, 111966. https://doi.org/10.1016/j.dyepig.2024.111966

[10] Miguel, M., Resende, I.S.P.D., Duraes, F., Pinto, M.M.M., Sousa, E. (2021). Xanthenes in Medicinal Chemistry: Synthetic strategies and biological activities. *European Journal of Medicinal Chemistry*, *210*, 113085. doi: 10.1016/j.ejmech.2020.113085

[11] Rajan, D., Rajamanikandan, R., Ilanchelian, M. (2023). Exploring the photophysical interaction of xanthene dyes with gold nanorods by optical spectroscopic techniques and *in-vitro* cytotoxicity studies of dye-nano conjugates. *Dyes and Pigments*, *220*, 111746. https://doi.org/10.1016/j.dyepig.2023.111746

[12] Cao, Y., He, P., wu, L., Shi, Y., Peng, Y., Zhang, S., Yang, X-F. (2024). Haloform-type reaction combined with the spirocyclic ring-opening of rhodamines affording a fluorescent probe for imaging hypochlorous acid in living organisms. *Sensors and Actuators B: Chemical*, *407*, 135384. https://doi.org/10.1016/j.snb.2024.135384

[13] Du, M., Zhang, Y., Xu, Z., Dong, Z., Zhao, S., Du, H., Zhao H. (2023). Point-of-Care and Dual-Response Detection of Hydrazine/Hypochlorite-Based on a Smart Hydrogel Sensor and Applications in Information Security and Bioimaging. *Molecules*, *28*(9), 3896. https://doi.org/10.3390/molecules28093896

[14] Guo, X., Wei, X-R., Sun, R., Xu, Y-J., Chen, Y., Ge, J-F. (2019). The optical properties of 9-amino-9H-xanthene derivatives in different pH and their application for biomarkers in lysosome and mitochondria. *Sensors and Actuators B: Chemical*, *296*, 126621. https://doi.org/10.1016/j.snb.2019.05.098

[15] Niu, G., Zhang, P., Liu, W., Wang, M., Zhang, H., Wu, J. Zhang, L., Wang, P. (2017). Near-Infrared Probe Based on Rhodamine Derivative for Highly Sensitive and Selective Lysosomal pH Tracking. *Analytical Chemistry*, *89*(3), 1922–1929. https://doi.org/10.1021/acs.analchem.6b04417

[16] Farat, O.K., Kovtun, A.V., Varenichenko, S.A., Mazepa, A.V., Markov, V.I. (2021). Novel rearrangement

of 1,3-benzo(naphtho)dioxin-4(1)-ones under Vilsmeier-Haack reagent. *Monatshefte für Chemie – Chemical Monthly*, *152*(1), 95–101. https://doi.org/10.1007/s00706-020-02733-z

[17] Farat, O.K., Varenichenko, S.A., Zaliznaya, E.V., Markov, V.I. (2020). Rearrangement of substituted 1,3-benzoxazines into xanthene-type compounds. *Ukrainian Chemistry Journal*, *2*, 111–122. https://doi.org/10.33609/0041-6045.86.2.2020.111-122

[18] Kovtun, A.V., Varenichenko, S.A., Zaliznaya, E.V., Mazepa, A.V., Farat, O.K., Markov, V.I. (2021). [Rearrangement of spiroderivatives of 1,3-benzo(naphtha)dioxin-4(1)-ones as a new method of synthesis of xanthenes bromoderivatives]. *Voprosy Khimii i Khimicheskoi Tekhnologii*, *4*, 73–77. (in Ukrainian). doi: 10.32434/0321-4095-2021-137-4-73-77

[19] Farat, O.K., Varenichenko, S.A., Markov, V.I. (2023). Synthesis and spectral properties of new xanthene-like fluorophore and light-filter. *Voprosy Khimii i Khimicheskoi Tekhnologii*, *3*. 110–115. https://doi.org/10.32434/0321-4095-2023-148-3-110-115

[20] Farat, O.K., Kovtun, A.V., Varenichenko, S.A., Mazepa, A.V., Markov, V.I. (2022). Novel xanthene-like dyes: synthesis and spectral properties. *Monatshefte für Chemie - Chemical Monthly*, *153*(5-6), 443–459. https://doi.org/10.1007/s00706-022-02931-x

[21] Varenichenko, S.A., Farat, O.K., Mazepa, A.V., Markov, V.I. (2019). Synthesis of new Schiff bases based on formyl derivatives of xanthenes. *Voprosy Khimii i Khimicheskoi Tekhnologii*, *5*, 22–26. http://dx.doi.org/10.32434/0321-4095-2019-126-5-22-26

[22] Reichardt, C. (2003). *Solvents and Solvent Effects in Organic Chemistry,* Weinheim: Wiley-VCH. doi: 10.1002/9783527632220

[23] Reichardt, C. (2006). Solvents and Solvent Effects: An introduction. *Organic Process Research & Development. 11*(1), 105–113. https://doi.org/10.1021/op0680082

[24] Brouwer, A.M. (2011). Standards for photoluminescence quantum yield measurements in solution (IUPAC Technical Report). *Pure Appl Chem*, *83*(12), 2213–2228. doi:10.1351/PAC-REP-10-09-31

[25] Fiedler, S., Frenzel, F., Würth, C., Tavernaro, I., Grüne, M., Schweizer, S., Engel, A., Resch-Genger, U. (2024). Interlaboratory Comparison on Absolute Photoluminescence Quantum Yield Measurements of Solid Light Converting Phosphors with Three Commercial Integrating Sphere Setups. *Analytical Chemistry*, *96*(17), 6730–6737. https://doi.org/10.1021/acs.analchem.4c00372