ABSTRACT: The fluorescence and other photophysical parameters of highly polarized, quadrupolar bis-coumarins possessing an electron-rich pyrrolo[3,2-b]pyrrole bridging unit are highly dependent on the linking position between both chromophores. Delocalization of the LUMO on the entire π-system results in intense emission and strong two-photon absorption.
reactivity toward the nucleophiles. To interrogate the role of the bridging position on the photophysical properties, absorption and emission measurements were carried out in three solvents differing in polarity (Figures 1 and 2, Table 1).

The differences in the spectroscopic properties of isomeric A−D−A dyes become visible by the naked eye (Coum6 - orange solid, Coum7 - red solid). Coum6 exhibits intense UV light absorption ($\lambda_{\text{abs}} = 358$ nm), whereas in the low-energy part of the absorption spectrum a weak, broad band can be observed ($\lambda_{\text{abs}} = 440$ nm). The opposite effect occurs in the case of Coum7, where strong absorption of yellow light ($\lambda_{\text{abs}} = 485$ nm) is accompanied by a residual absorption of UV radiation. In accordance with the centrosymmetric architecture, there is no solvatochromism in these dyes; however, a significant drop of absorption coefficient is observed while the polarity of the solvent increases (Figures 1 and 2).

There are two strong analogies between the above-described characteristics and photophysics of simpler D−A coumarins. First, in Coum6 the Stokes shift is large whereas there is only a moderate difference between the absorption and emission in the case of Coum7. Moreover, for Coum6 a very weak red fluorescence is observed, while Coum7 has strong emission (Table 1). It should also be mentioned that, for more polar solvents, the Coum6 emission is below the detection limit. On the other hand, changing the substitution position on the coumarin subunit from 6 to 7 results in a 650-fold increase in the fluorescence quantum yield from 0.06% to 39% in toluene. Due to the incomparably stronger emissive properties, in the case of Coum7, solvatofluorochromism can be observed indicating excited-state symmetry-breaking.20 The successive increase in the solvent polarity results in a clear Stokes shift, from 3000 cm$^{-1}$ in toluene to 5300 cm$^{-1}$ in DMSO. The described phenomenon is also accompanied by a significant decrease of the fluorescence quantum yield, down to 0.02% in DMSO.

In principle the photophysical properties of these quadrupolar bis-coumarins mirror the properties of 7-amino-coumarins vs 6-aminocoumarins; i.e., coumarins possessing electron-donating groups at the 6-position have weak but bathochromically shifted emission whereas coumarins substituted at the 7-position exhibit strong emission.

From a purely structural perspective the investigated dyes can be considered as bis-coumarins and, at the same time, as centrosymmetric pyrrolo[3,2-b]pyrroles. The photophysical properties of Coum6 and Coum7 can be directly compared to bis-2,5-(4-cyanophenyl)pyrrolo[3,2-b]pyrrole,18 which is the prototypical A−D−A pyrrolo[3,2-b]pyrrole. Absorption of Coum7 is bathochromically shifted by ca. 80 nm and the emission by over 120 nm, which reveals that the coumarin scaffolds affect the electron structure making it a truly π-expanded system. On the other hand, the main absorption...
band of Coum6 is hypsochronically shifted ca. 50 nm in comparison to bis-2,5-(4-cyanophenyl)pyrrolo[3,2-\text{b}]pyrrole.

The investigated dyes A→D→A architecture encouraged us to explore their two-photon absorption (TPA) properties, as A→D→A is one of the most successful motifs of TPA dyes. The TPA spectra were measured using a femtosecond open-aperture Z-scan method\textsuperscript{21,22} in a MeTHF (Figure 3). Coum7 was found to have a strong and broad TPA peak centered at 12 000 cm\textsuperscript{-1} (840 nm) with the peak TPA cross section equal to 850 ± 160 GM, where 1 GM = 10\textsuperscript{-50} cm\textsuperscript{4} s photon\textsuperscript{-1} molecule\textsuperscript{-1}. The two-photon absorption cross section increased even further starting from 650 nm toward the blue edge of the spectrum, while the \(\sigma(2)\) reached 4000 ± 430 GM at 17 500 cm\textsuperscript{-1} (453 nm). In contrast, Coum6 showed a much weaker TPA, with \(\sigma(2)\) \(\leq\) 10 GM for 9500–15000 cm\textsuperscript{-1} (1050–660 nm). The spectral magnitude was monotonically increased at the photon energy higher than 15 000 cm\textsuperscript{-1} (Figure S17); nevertheless, the maximum value observed was \(\sigma(2)\) = 100 ± 26 GM at 17 500 cm\textsuperscript{-1} (453 nm), which is in 40-fold contrast to that of Coum7.

The TPA peak of Coum7 at 12 000 cm\textsuperscript{-1} (i.e., 24 000 cm\textsuperscript{-1} in the transition energy) did not match the transition energy produced by the one-photon absorption peak (Figure 2). This behavior can be understood using Laporte’s selection rule complementary for one- and two-photon absorption. The significant increase observed at higher energies likely originates from a resonance enhancement\textsuperscript{23}.

In order to investigate the effect of the coumarin substitution site on the photophysical properties, we combined our experimental results with TD-DFT calculations (including optimization of structures) using different functionals and basis sets (see Supporting Information (SI) for details). We note that the use of the standard TD DFT/B3LYP/6-31G(d,p) approach in the case of CT systems like Coum6 and Coum7 is insufficient to properly reproduce the photophysical properties. To obtain better agreement between experiment and computational results, hybrid functionals with an increased amount of Hartree-Fock exchange, such as B3LYP-37, should be used. Calculated energies of electronic transitions with that functional are shown in Table 2. Small differences between experiment and calculations result from the limitations of the TD-DFT method and from the fact that molecules used in calculations do not possess alkyl chains at phenyl and carboxyl subunits.

As can be seen in the table, the oscillator strength of the \(S_0 \rightarrow S_1\) transition in Coum6 is much lower (\(f = 0.062\)) compared to the \(S_0 \rightarrow S_1\) transition in Coum7 (\(f = 2.089\)) which indicates the effectively forbidden character of the Coum6 first electron transition, leading to a lack of absorption in the yellow region. On the other hand, the Coum7 absorption spectra are bathochromically shifted compared to Coum6, which is in line with the computational results. Moreover, the observed strong absorption in the UV range for Coum6 corresponds to the allowed \(S_0 \rightarrow S_2\) transition (\(f = 1.914\)). Due to the fact that the \(S_0 \rightarrow S_1\) as well as the \(S_1 \rightarrow S_2\) transitions are mainly described by HOMO/LUMO configurations, the two transitions possess similar properties; thus the forbidden nature of the \(S_0 \rightarrow S_1\) transition also manifests in the emissive properties of Coum6. However, an analysis of fluorescence spectra of investigated A→D→A systems indicates that, in the case of Coum6, a much larger Stokes shift is observed, compared to Coum7.

HOMOs of both Coum6 and Coum7 are mainly located on the electron-rich pyrrolo[3,2-\text{b}]pyrrole core (Figure 4). On the other hand, clear differences of the electron density can be observed for LUMOs. In the case of Coum6, the LUMO is completely located on the electron-accepting coumarin subunits, while the Coum7 LUMO orbital is also localized on the central pyrrolopyrrole core. Such shapes of the frontier orbitals indicate that the \(S_0 \rightarrow S_1\) transitions in Coum6 and Coum7 are intramolecular charge-transfer (CT) transitions from D to the two \(A\) centers, with a lesser degree of charge transfer in Coum7 (see SI for quantitative data). Moreover, upon excitation of Coum6, a better charge separation is observed (see SI for quantitative data). The larger charge

\[\text{Table 2. PCM/B3LYP-37/6-31G(d,p) Calculation Results of Coum6 and Coum7 Electronic Transitions in Toluene}^a\]

| Transition        | Coum6 \(\lambda\) [nm] \((f)\) | Coum7 \(\lambda\) [nm] \((f)\) |
|------------------|-------------------------------|-------------------------------|
| \(S_0 \rightarrow S_1\) | 448 (0.062)                   | 475 (2.089)                   |
| \(S_0 \rightarrow S_2\) | 448 (0.000)                   | 397 (0.000)                   |
| \(S_0 \rightarrow S_3\) | 342 (1.914)                   | 354 (0.051)                   |
| \(S_1 \rightarrow S_2\) | 338 (0.000)                   | 319 (0.000)                   |
| \(S_1 \rightarrow S_3\) | 338 (0.055)                   | 315 (0.000)                   |
| \(S_2 \rightarrow S_3\) | 598 (0.017)                   | 535 (2.441)                   |

\(^a\)Wavelengths (\(\lambda\)) and oscillator strengths (\(f\)) of the \(S_0 \rightarrow S_1\) electronic transitions.
separation in the Coum6 S1 excited state leads to significant Coulomb interaction driven stabilization, manifested by the lower energy of the S1 → S0 transition and a significant drop in oscillator strength (f = 0.062) with regard to Coum7 (f = 2.089). On the other hand, a much weaker charge separation in the Coum7 S1 state, caused by the significant delocalization of the LUMO over both the pyrrolo[3,2-b]pyrrole core and the coumarin subunits, leads to a greater oscillator strength of the S1 → S0 transition.

A simulation of the TPA spectrum successfully reproduced the contrast features of Coum6 and Coum7 (Figure S5). For Coum6 the transition intensity is weak for transitions up to S0, with strong TPA transitions only existing for those to higher excited states. In contrast, for Coum7, a strong transitions to S1 appeared at 770 nm, which corresponds to the experimentally observed TPA peak centered at 840 nm (Figure 3), though it is energetically overestimated. Calculation results also show complementary behavior of one- and two-photon transitions for these centrosymmetric molecules. Weak or no TPA transitions were observed to the excited states to which one-photon transitions are strong (S0 → S1 for Coum6 and S0 → S2 for Coum7) as well as vice versa (S0 → S2 of Coum7 is a strong TPA transition but forbidden for one-photon absorption).

By applying the concept of electron donor–acceptor systems,24 the differences between the transition energies and oscillator strengths for the excitation and fluorescence of Coum6 and Coum7 can be assigned to the differentiation of short-range interactions within the AD junction. This is in line with the results of Liu and co-workers for 6-aminocoumarins.25 The calculated solvent shifts of the transition energies, along with the increase of solvent polarity, are in good agreement with those observed (see SI). There is however no clear explanation for the observed decrease of fluorescence yield of Coum7 in polar DMSO. This suggests an opening of the nonradiative decay pathway and requires the use of increasingly sophisticated models of solvent effects for CT systems.26-28

Both the quadrupolar architecture of the hybrid dyes and the bridging position of the coumarin scaffolds with the electron-rich pyrrolo[3,2-b]pyrrole unit play decisive roles in the optoelectronic properties of the new dyes. In analogy to the classical 7-dialkylaminocoumarins, the emission of the quadrupolar bis-coumarin with a pyrrolo[3,2-b]pyrrole unit at the seventh position is strong and moderately bathochromically shifted. Shifting the bridge to the position 6 drastically changes the nature of the LUMO, resulting in its localization solely on the coumarin subunits. This results in a weakly emitting dye with $\lambda_{\text{em}}^{\text{max}}$ at 650 nm. Marked differences in their two-photon absorbing properties (TPA cross-section in the near-infrared region decreased from 850 GM for Coum7 to less than 10 GM for Coum6) are also caused by the diversity of the LUMO distribution.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c02349.

Quantum chemical calculation and photophysical experimental data, and synthetic procedures, as well as 1H and 13C{1H} NMR spectra (PDF)

AUTHOR INFORMATION

Corresponding Authors

Kenji Kamada – Nanomaterials Research Institute (NMRI), National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan; Department of Chemistry, Graduate School of Science and Technology, Kwansei Gakuin University, Sanda 669-1337, Japan; orcid.org/0000-0002-1763-9383; Email: hagren@kth.se

Hans Ågren – Department of Physics and Astronomy, Uppsala University, SE-751 20 Uppsala, Sweden; orcid.org/0000-0002-1763-9383; Email: hagren@kth.se

Daniel T. Gryko – Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland; orcid.org/0000-0002-2146-1282; Email: dtgryko@icho.edu.pl

Authors

Krzysztof Górski – Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland; orcid.org/0000-0002-6439-2651

Irena Depereińska – Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland

Glib V. Baryshnikov – Laboratory of Organic Electronics, Department of Science and Technology, Linköping University, SE-60174 Norrköping, Sweden; orcid.org/0000-0002-0716-3385

Shuhei Ozaki – Nanomaterials Research Institute (NMRI), National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan; Department of Chemistry, Graduate School of Science and Technology, Kwansei Gakuin University, Sanda 669-1337, Japan

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.1c02349

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the Foundation for Polish Science (TEAM POIR.04.04.00-00-3CF4/16-00). We also thank Global Research Laboratory Program (2014K1A1A2064569) through the National Research Foundation (NRF) funded by Ministry of Science, ICT & Future Planning (Korea) and the National Science Centre, Poland, under QuantERA programme, Project 2017/25/Z/ST2/03038. G.V.B. acknowledges the financial support of the Swedish Research Council (Starting Grant No. 2020-04600). The quantum-chemical calculations were performed with computational resources provided by Swedish National Infrastructure for Computing (SNIC 2020-3-29) at the High-Performance Computing Center North (HPC2N) partially funded by the Swedish Research Council through the Grant Agreement No. 2018-05973. Theoretical calculations were also performed at the Interdisciplinary Centre of Mathematical and Computer Modelling (ICM) of the Warsaw University under the computational grant G-32-10. This work was partially supported by JSPS KAKENHI Grant Number 21H01887(KK).
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