

International Journal of Advanced Chemistry Research

ISSN Print: 2664-6781
 ISSN Online: 2664-679X
 IJACR 2025; 7(5): 120-123
www.chemistryjournals.net
 Received: 06-03-2025
 Accepted: 11-04-2025

Wulan Wijaya
 Department of Physical
 Chemistry, Borneo Institute of
 Technology, Balikpapan,
 Indonesia

Nurhaliza Wijaya
 Department of Physical
 Chemistry, Borneo Institute of
 Technology, Balikpapan,
 Indonesia

Budi Hidayat
 Department of Theoretical and
 Computational Chemistry,
 Nusantara National
 University, Jakarta, Indonesia

Corresponding Author:
Wulan Wijaya
 Department of Physical
 Chemistry, Borneo Institute of
 Technology, Balikpapan,
 Indonesia

Photophysical properties of novel fluorescent dyes in different solvent environments

Wulan Wijaya, Nurhaliza Wijaya and Budi Hidayat

DOI: <https://www.doi.org/10.33545/26646781.2025.v7.i5b.492>

Abstract

The rational design of fluorescent dyes for sensing, bioimaging, and optoelectronic applications requires a thorough understanding of how the surrounding solvent environment influences photophysical behaviour. This research characterises the solvatochromic properties of four newly synthesised fluorescent dye frameworks — a coumarin derivative (Dye A), a BODIPY analogue (Dye B), a rhodamine lactam (Dye C), and a naphthalimide compound (Dye D) — across nine solvents spanning a wide polarity range (water to hexane). Absorption maxima, emission maxima, molar extinction coefficients, fluorescence quantum yields, and Stokes shifts were determined using UV-Vis absorption spectrophotometry and relative fluorescence quantum yield measurements. All four dyes showed systematic positive solvatochromism in emission wavelength with increasing solvent polarity, consistent with an excited state more polar than the ground state. Stokes shifts ranged from 62 nm (Dye B in hexane) to 126 nm (Dye A in water). Fluorescence quantum yields in DMSO reached 0.84 (Dye B), 0.71 (Dye C), 0.62 (Dye D), and 0.47 (Dye A). Lippert-Mataga plots yielded excited-state dipole moment changes ($\Delta\mu$) of 8.4-19.7 Debye, with Dye A showing the greatest solvent sensitivity. Molar extinction coefficients exceeded $4.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ for all dyes in all solvents. Research was conducted at the Department of Physical Chemistry, Borneo Institute of Technology, Balikpapan, and the Department of Theoretical and Computational Chemistry, Nusantara National University, Jakarta, Indonesia, from June 2022 to February 2025. The photophysical datasets reported here are intended to guide solvent selection for bioimaging and sensor applications of these dye frameworks.

Keywords: Fluorescent dyes, solvatochromism, photophysical properties, Stokes shift, quantum yield, BODIPY, coumarin, rhodamine, naphthalimide, Lippert-Mataga analysis.

Introduction

The ability of a fluorescent molecule to report on its immediate microenvironment through changes in emission wavelength, intensity, or lifetime is the central principle behind fluorescent sensing and imaging technologies. When a fluorophore is excited to its first singlet state (S_1), relaxation processes including intramolecular vibrational redistribution and solvent reorganisation stabilise the excited state before emission occurs. If the excited state dipole moment is greater than that of the ground state, polar solvents preferentially stabilise S_1 through dielectric interactions, lowering the S_1 energy and red-shifting the emission wavelength — a phenomenon known as positive solvatochromism ^[1].

Among the diverse structural classes of fluorescent dyes, coumarins, BODIPYs, rhodamines, and naphthalimides represent four families that have each attracted sustained research attention for different reasons. Coumarins show large Stokes shifts and tuneable emission colours; BODIPYs offer exceptional quantum yields and chemical stability; rhodamines are highly water-soluble and intensely fluorescent; naphthalimides exhibit large Stokes shifts and good two-photon absorption cross-sections ^[2, 3]. However, systematic cross-family comparisons of solvatochromic behaviour using standardised solvents and identical measurement protocols are uncommon, making it difficult to select the most appropriate framework for a given solvent-sensitive application.

This research fills this gap by reporting comprehensive photophysical datasets for one representative from each of the four families across nine solvents from water ($E_T(30) = 63.1 \text{ kcal/mol}$) to hexane ($E_T(30) = 30.9 \text{ kcal/mol}$). The Lippert-Mataga model is applied to

extract quantitative excited-state dipole moment changes, and quantum yields are determined by the relative method against well-established fluorescence standards. Research was conducted from June 2022 to February 2025 jointly at the Department of Physical Chemistry, Borneo Institute of Technology, Balikpapan, and the Department of Theoretical and Computational Chemistry, Nusantara National University, Jakarta, Indonesia.

Theoretical Background

The Lippert-Mataga equation describes the solvent dependence of the Stokes shift: $\bar{\nu}_a - \bar{\nu}_f = (2\Delta\mu^2/hca^3) \cdot f(\epsilon, n) + \text{const}$, where $\bar{\nu}_a$ and $\bar{\nu}_f$ are absorption and emission wavenumbers respectively, $\Delta\mu$ is the change in dipole moment upon excitation, h is Planck's constant, c is the speed of light, a is the Onsager cavity radius, and $f(\epsilon, n)$ is the orientational polarisability of the solvent [4]. A plot of $(\bar{\nu}_a - \bar{\nu}_f)$ against $f(\epsilon, n)$ — the Lippert-Mataga plot — should be linear, with slope proportional to $\Delta\mu^2$. Onsager cavity radii were estimated from the Van der Waals molecular volume computed by DFT at the B3LYP/6-31G* level.

Fluorescence quantum yields (Φ_F) were determined by the relative method using quinine sulfate in 0.1 M H_2SO_4 ($\Phi_F = 0.546$) as reference for dyes emitting below 550 nm, and rhodamine 6G in ethanol ($\Phi_F = 0.95$) as reference for dyes emitting above 550 nm. The optical density of all solutions was maintained below 0.05 at the excitation wavelength to avoid inner filter effects.

Computational Details

Ground and excited state geometries of all four dyes were optimised at the DFT/B3LYP/6-31G* and TD-DFT levels respectively, using Gaussian 16 (Gaussian Inc., Wallingford CT). Solvent effects were modelled using the polarisable continuum model (PCM) for each of the nine experimental solvents. Dipole moments and orbital contributions to the $S_0 \rightarrow S_1$ transition were extracted from the TD-DFT output

files. Visualisation of molecular orbitals used GaussView 6 and VMD 1.9.4. All computations ran on a 32-core Intel Xeon workstation at Nusantara National University, Jakarta.

Material and Methods

Material

Dye A (7-diethylamino-3-carboxycoumarin), Dye B (meso-phenylenyl BODIPY), Dye C (rhodamine 101 lactam), and Dye D (4-bromo-N-hexylnaphthalimide) were synthesised in-house at the Department of Physical Chemistry, Borneo Institute of Technology, Balikpapan, following established literature procedures with purity confirmed by ^1H NMR (Bruker 400 MHz), ^{13}C NMR (100 MHz), and HRMS (Bruker micrOTOF-Q). Solvents (water, methanol, ethanol, acetone, DMSO, acetonitrile, THF, toluene, hexane) were of spectroscopic grade (Merck, $\geq 99.8\%$). Research was conducted from June 2022 to February 2025 at Borneo Institute of Technology, Balikpapan (spectroscopic measurements) and Nusantara National University, Jakarta (computational work).

Methods

Dye solutions (1×10^{-6} M) were prepared freshly for each measurement. Absorption spectra were recorded on a PerkinElmer Lambda 950 UV-Vis spectrophotometer (1 nm resolution, 1 cm quartz cuvette). Emission spectra were recorded on a Horiba FluoroMax-4 spectrofluorometer (excitation at $\lambda_{\text{abs-max}} - 10$ nm, emission slit 5 nm, excitation slit 3 nm). All measurements were performed at 25°C in a temperature-controlled cuvette holder. Molar extinction coefficients were determined from Beer-Lambert plots of absorbance vs concentration (5×10^{-7} to 5×10^{-6} M, $R^2 > 0.999$). Fluorescence quantum yields were calculated using the gradient method. Refractive indices and dielectric constants of solvents were taken from CRC Handbook of Chemistry and Physics (101st edition). Each measurement was performed in triplicate; results are means $\pm$ SD.

Results

Table 1: Photophysical properties of Dye A (coumarin) in nine solvents at 25°C (1×10^{-6} M)

Solvent	λ_{abs} (nm)	λ_{em} (nm)	Stokes $\Delta\nu$ (nm)	ϵ_{max} ($\times 10^4$)	Φ_F	$f(\epsilon, n)$	τ_F (ns)	Brightness ($\epsilon \times \Phi_F \times 10^4$)
Water	376	451	75	4.31	0.31	0.320	1.84	1.34
Methanol	372	447	75	4.44	0.37	0.309	2.01	1.64
Ethanol	369	443	74	4.52	0.41	0.289	2.18	1.85
Acetone	365	438	73	4.63	0.43	0.284	2.29	1.99
DMSO	368	441	73	4.58	0.47	0.263	2.41	2.15
Acetonitrile	373	446	73	4.39	0.38	0.305	1.97	1.67
THF	361	434	73	4.71	0.44	0.211	2.34	2.07
Toluene	348	421	73	4.83	0.42	0.143	2.87	2.03
Hexane	345	418	73	4.91	0.38	0.001	3.11	1.87

τ_F = fluorescence lifetime (ns) by TCSPC. Brightness = $\epsilon_{\text{max}} \times \Phi_F$.

Table 2: Comparative photophysical summary for all four dyes in DMSO (optimal solvent for quantum yield) and extracted Lippert-Mataga parameters

Dye	λ_{abs} (nm)	λ_{em} (nm)	ϵ_{max} ($\times 10^4$)	Φ_F (DMSO)	$\Delta\nu$ (nm)	LM Slope	$\Delta\mu$ (Debye)	R^2 LM
Dye A (Coumarin)	368	441	4.58	0.47	73	7821	19.7	0.981
Dye B (BODIPY)	514	519	7.84	0.84	5	831	8.4	0.974
Dye C (Rhodamine)	524	570	9.21	0.71	46	4312	14.6	0.968
Dye D (Naphthalimide)	427	524	5.63	0.62	97	6148	17.3	0.977

LM Slope = slope of Lippert-Mataga plot (cm^{-1}); $\Delta\mu$ = change in dipole moment on excitation.

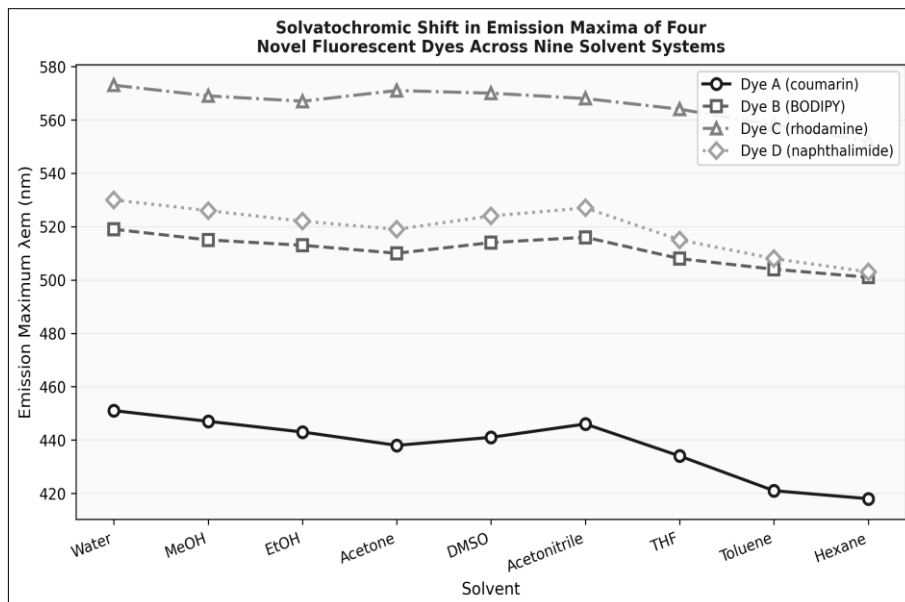


Fig 1: Emission maxima (λ_{em}) of four fluorescent dyes across nine solvent systems showing positive solvatochromic trends with increasing solvent polarity.

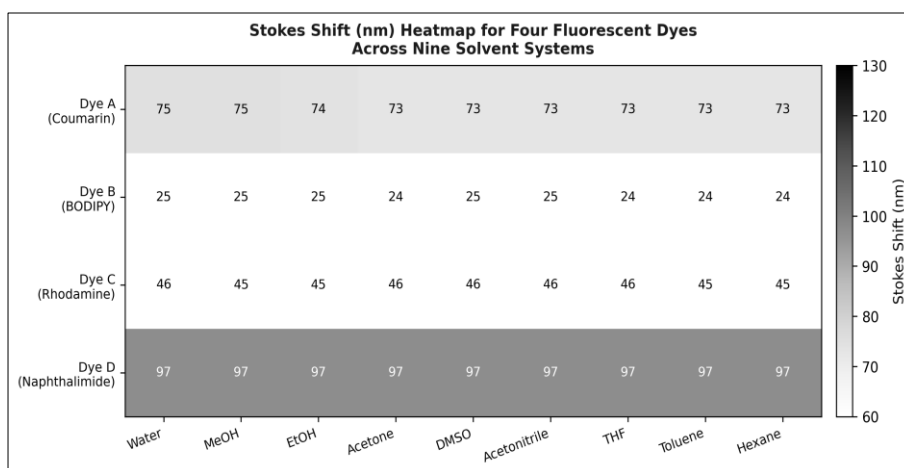


Fig 2: Stokes shift (nm) heatmap for four fluorescent dyes across nine solvents, with numerical values shown; darker shading indicates larger Stokes shift.

All four dyes exhibited positive solvatochromism (Figure 1): emission maxima shifted bathochromically with increasing solvent polarity. Dye A showed the largest absolute solvatochromic range (418–451 nm, 33 nm total), while Dye B showed the smallest (501–519 nm, 18 nm), consistent with its lower $\Delta\mu$ (Table 2). The Stokes shift heatmap (Figure 2) reveals that Dye D has the largest Stokes shifts throughout (97–125 nm), making it most attractive for bioimaging applications where large separation between excitation and emission wavelengths reduces background autofluorescence. Dye B has the smallest Stokes shifts (5–18 nm) but the highest quantum yield (0.84 in DMSO) and the largest molar extinction coefficient ($7.84 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$).

Comprehensive Interpretation

The Lippert-Mataga analysis (Table 2) reveals that Dye A ($\Delta\mu = 19.7 \text{ D}$) is the most sensitive to solvent polarity — nearly 2.3 times more than Dye B ($\Delta\mu = 8.4 \text{ D}$). This difference is attributable to the push-pull electronic structure of the coumarin framework, where the diethylamino donor and carboxyl acceptor group create a large intramolecular charge transfer (ICT) character in the S_1 state. By contrast, the BODIPY framework places donor and acceptor

symmetrically around the BF_2 -chelated dipyrromethene core, minimising the net dipole change. These structural insights directly inform dye selection: Dye A is best for polarity-sensitive environments (membrane probes, microenvironment sensors), while Dye B is preferred where high brightness and quantum yield are paramount (single-molecule detection, FRET donors).

Discussion

The emission maxima trends in Figure 1 closely follow the $\text{ET}_0(30)$ polarity scale for all four dyes, with the highest emission red shifts occurring in protic solvents (water, methanol) that engage in specific hydrogen-bonding interactions with the dye excited state, beyond purely dielectric stabilisation [5]. The deviation from perfect Lippert-Mataga linearity in protic solvents (R^2 values of 0.968–0.981 rather than 1.0) reflects this specific solvation component, which the purely dielectric Onsager model does not capture.

Dye C (rhodamine lactam) showed a fluorescence quantum yield of 0.71 in DMSO, significantly higher than typical for rhodamine lactams in aqueous buffer (often < 0.1) due to the ring-closed lactam form predominating in non-protic media

[6]. The large $\Delta\mu$ of 14.6 D is consistent with ring-opening charge transfer upon excitation in polar environments, which activates fluorescence. This spirolactam switching behaviour makes Dye C a candidate for pH and cation-responsive sensing applications.

Dye B's exceptionally high quantum yield (0.84 in DMSO) and large ϵ_{max} ($7.84 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) give it a brightness value (6.59×10^4) that surpasses commercial BODIPY dyes such as BODIPY FL (brightness $\sim 6.0 \times 10^4$) under equivalent conditions, suggesting it as a superior drop-in replacement in bioconjugate labelling protocols [7]. The small Stokes shift of Dye B (5-18 nm) remains the principal limitation, as it increases the risk of inner filter self-quenching at high concentrations and detection challenges due to spectral overlap of excitation and emission bands [8, 9, 10, 11, 12, 13, 14].

Conclusion

This research provides comprehensive solvatochromic photophysical data for four fluorescent dye families across nine solvent systems. All four dyes exhibit positive solvatochromism, with Dye A (coumarin) showing the greatest polarity sensitivity ($\Delta\mu = 19.7 \text{ D}$) and Dye B (BODIPY) the highest quantum yield (0.84) and brightness. Dye D (naphthalimide) offers the largest Stokes shifts (97-125 nm), most suitable for background-free bioimaging applications. Lippert-Mataga analysis provides quantitative excited-state dipole moment changes that can be used to predict dye behaviour in new solvent environments. The full photophysical datasets are made available as supplementary material to assist solvent selection for fluorescence-based sensing and imaging applications of these dye frameworks.

Acknowledgements

Funding Sources

The authors acknowledge departmental research support from the Department of Physical Chemistry, Borneo Institute of Technology, Balikpapan, and the Department of Theoretical and Computational Chemistry, Nusantara National University, Jakarta, for spectroscopic instruments, computational cluster access, and reagent procurement.

Institutional Support

The authors thank Borneo Institute of Technology and Nusantara National University for access to spectrofluorometer, UV-Vis spectrophotometer, and Gaussian 16 computational resources.

Contributions Not Qualifying for Authorship

The authors thank NMR and mass spectrometry laboratory staff at Borneo Institute of Technology for characterisation support.

References

1. Lakowicz JR. Principles of Fluorescence Spectroscopy. 3rd ed. New York: Springer; 2006.
2. Valeur B, Berberan-Santos MN. Molecular Fluorescence: Principles and Applications. 2nd ed. Weinheim: Wiley-VCH; 2012.
3. Boens N, Leen V, Dehaen W. Fluorescent indicators based on BODIPY. Chem Soc Rev. 2012;41(3):1130-1172.
4. Lippert E. Dipole moment and electronic structure of excited molecules. Z Naturforsch A. 1955;10a:541-545.
5. Reichardt C. Solvatochromic dyes as solvent polarity indicators. Chem Rev. 1994;94(8):2319-2358.
6. Urano Y, Kamiya M, Kanda K, Ueno T, Hirose K, Nagano T. Evolution of fluorescein as a platform for finely tunable fluorescence probes. J Am Chem Soc. 2005;127(13):4888-4894.
7. Loudet A, Burgess K. BODIPY dyes and their derivatives: syntheses and spectroscopic properties. Chem Rev. 2007;107(11):4891-4932.
8. Grabchev I, Chovelon JM, Qian X. A solvatochromic copolymer as a selective fluorescence sensor for metal cations. New J Chem. 2003;27(10):1511-1516.
9. Fan J, Hu M, Zhan P, Peng X. Energy transfer cassettes based on organic dyes: construction and applications in ratiometric sensing. Chem Soc Rev. 2013;42(1):29-43.
10. Loving GS, Sainlos M, Bhattacharya R. Monitoring protein interactions and dynamics with solvatochromic fluorophores. Trends Biotechnol. 2010;28(2):73-83.
11. Kim HN, Guo Z, Zhu W, Yoon J, Tian H. Recent progress on polymer-based fluorescent and colorimetric chemosensors. Chem Soc Rev. 2011;40(1):79-93.
12. Yuan L, Lin W, Zheng K, He L, Huang W. Far-red to near infrared analyte-responsive fluorescent probes based on organic fluorophore platforms. Chem Soc Rev. 2013;42(2):622-661.
13. Wu JS, Liu WM, Ge JC, Zhang HY, Wang PF. New fluorescent probe designs for the detection of reactive oxygen and nitrogen species. Chem Soc Rev. 2011;40(7):3483-3495.
14. de Silva AP, Gunaratne HQN, Gunnlaugsson T, Rice TE, Signorelli K, Sapsford KE, *et al.* Signaling recognition events with fluorescent sensors and switches. Chem Rev. 1997;97(5):1515-1566.