



Superradiant properties of 4,4'-bis(1*H*-phenanthro[9,10-*d*]imidazol-2-yl)biphenyl and how a laser dye with exceptional stability can be obtained in only one synthetic step

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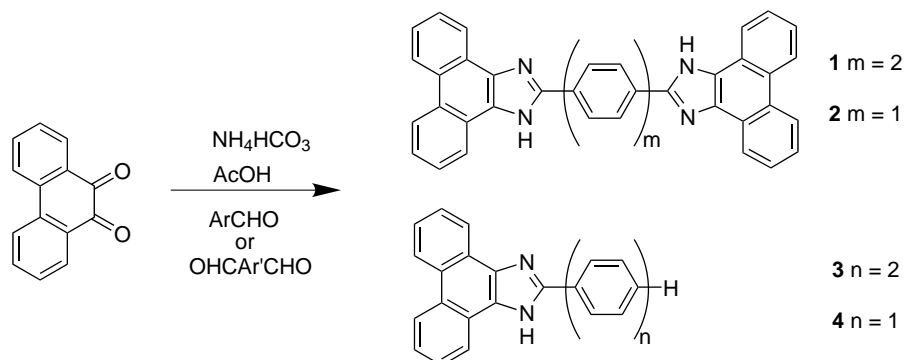
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Abstract—The extremely facile synthesis of a very stable laser dye with superradiant properties is reported. The laser action of the dye is demonstrated through a transverse pumping scheme with the advantage that no elaborate laser resonator is required due to the very high gain of the laser medium. The emitted light exhibits speckle, spatial coherence and the ability to be collimated by a lens. © 2001 Elsevier Science Ltd. All rights reserved.

Laser dyes have been the subject of intense study from both the synthetic and photophysical viewpoint.¹ Laser dyes have, in terms of applicability, served the purpose of extending the range of wavelengths accessible to traditional laser systems (solid state or gas discharge). Traditionally, the pulsed laser system is used as a pumping source with the dye laser compound dissolved in a suitable solvent. It is then possible to tune the wavelength of the laser light by use of a cavity and further still by the correct choice of substituents on the laser dye and solvent. One of the shortcomings of this approach is that most laser dyes are complex organic molecules that deteriorate or break down when illumi-

nated with the large intensity of a pumping laser. The complexity of the organic dye molecules is also synonymous with a high cost and therefore dye molecules with a high stability and a low cost are desirable. Often the traditional dyes have only a moderate optical gain and elaborate longitudinal pumping schemes are required.² Due to the nature of the dye, it is postulated that it may also be used as a dopant in a polymer-based dye laser.³

In this report, we describe how the 1*H*-phenanthro[9,10-*d*]imidazol-2-yl group is easily realized as a substituent in the 4,4'-positions of biphenyl as shown in Scheme 1 and the application of the substituent in



Scheme 1.

Keywords: laser dyes; lasers; optical pumping; X-ray crystallography.

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making laser dyes. The reaction works for any aromatic system containing an aldehyde group, provided that no basic groups are present, and proceeds from phenanthrenequinone, a source of ammonia and the aldehyde in acetic acid, as a fast, and efficient one-step reaction.

When two 1*H*-phenanthro[9,10-*d*]imidazol-2-yl groups are attached to biphenyl or benzene the title compounds 4,4'-bis(1*H*-phenanthro[9,10-*d*]imidazol-2-yl)biphenyl **1** and 1,4-bis(1*H*-phenanthro[9,10-*d*]imidazol-2-yl)benzene **2** were obtained in good yield. When only one chromophore was attached 4-(1*H*-phenanthro[9,10-*d*]imidazol-2-yl)biphenyl **3** and (1*H*-phenanthro[9,10-*d*]imidazol-2-yl)benzene **4** were likewise obtained in

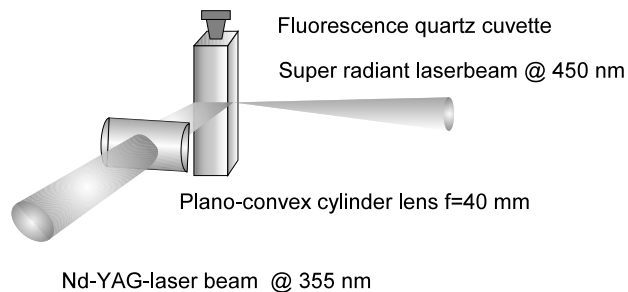


Figure 1. Details of the transverse pumping set-up.

good yield. The crude products were sufficiently pure for use in the optical studies. The synthesis of compounds **2**,⁴ **3**⁵ and **4**⁶ has been reported earlier while photophysical data (UV-vis in ethanol⁷ and methanol⁸ and fluorescence in the solid⁹) has been reported for **4** only.

When saturated solutions in THF were subjected to a transversal pumping scheme using a pulsed Nd-YAG UV laser at a wavelength of 355 nm as shown in Fig. 1 superradiant laser properties were observed. Interestingly, of compounds **3** and **4** only the former was found to be able to operate as a superradiant laser dye. Compounds **2** and **3** are not nearly as efficient as **1**.

A very sharp laser line at 450 nm is produced as shown in Fig. 2 (FWHM = 2 nm). We ascribe this remarkable effect to the large degree of conjugation and rigidity observed for this compound and further present the crystal structures of compounds **1**, **3** and **4** to support this statement. The geometry of the molecules in the solid state is planar as shown for **1** in Fig. 3. This is very unusual for biphenyl systems in general. In the solid both compounds **1** and **3** crystallize with solvent through hydrogen bonding with the imidazole nitrogen

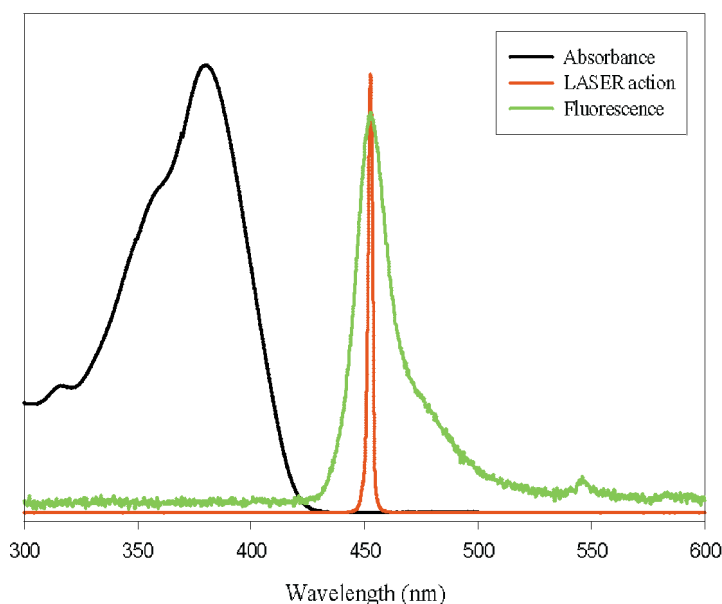


Figure 2. An overview of the photophysical data showing the absorbance of compound **1** (black line), the narrow peak observed with LASER action of compound **1**. When the incident light is attenuated the sharp laser peak becomes broader and weakens in intensity. The shape of the emission curve gradually approaches that of the fluorescence spectrum obtained in the same setup with a diluted sample of compound **1**. The scale is arbitrary and different for each of the three traces, the illustration is meant to indicate the position in wavelength and the shape of the curves.



Figure 3. A stereoview of compound **1** emphasizing the planar conformation in the solid state.

atoms, whereas compound **4** crystallizes with no solvent.

An indication of the efficiency of the lasing is given relative to Coumarin 120 (7-amino-4-methylcoumarin), a well-known laser dye that operates in the same wavelength region. Compound **1** is in qualitative terms more efficient than C120 under optimal conditions for the two (**1** in THF and C120 in methanol). In particular, the effect known as superradiance (vide supra) has been observed from the dyes. This is an indicator of a highly efficient laser dye. When pumping the laser dye in the experimental setup as shown in Fig. 1 with an attenuation of the incident laser light the fluorescence spectrum of **1** was observed (see Fig. 2). Upon increasing the intensity of the incident laser light the shape of the emission curve produced by the sample was seen to narrow and give rise to a sharp laser line from the sample (as described above). The UV–vis spectra shown in Table 1 are in good agreement with the chemical structure of the synthesized dyes.

In summary, we have in this paper described the simple synthesis of a remarkably efficient laser dye containing the 1*H*-phenanthro[9,10-*d*]imidazol-2-yl group and further described the general applicability of this group to laser dyes by example. We have also reported the crystal structures and general photophysical data for this series of compounds and reported the results from

experiments demonstrating the properties of the compounds when applied as laser dyes. Further, comparison with a known reference laser dye shows that the title compound is superior in both chemical stability and efficiency.

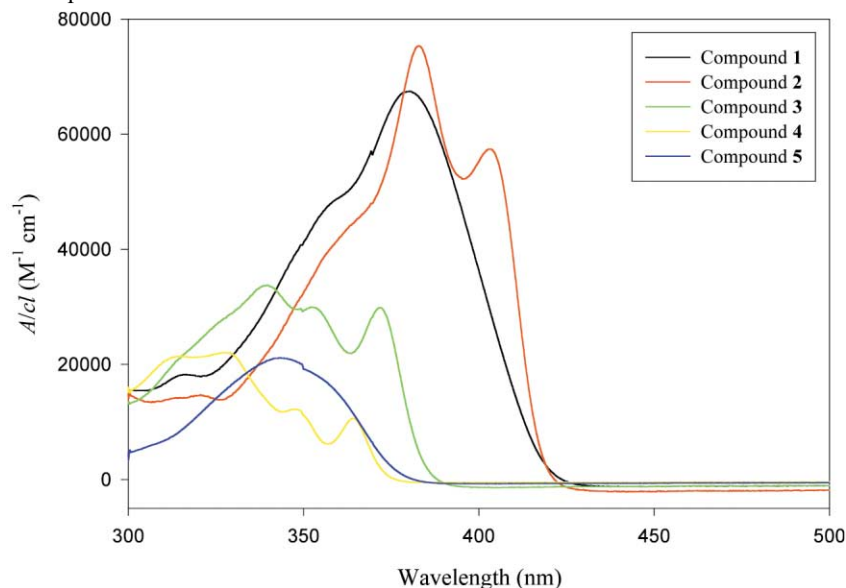
1. Experimental procedures

In the ^{13}C NMR spectrum of compound **1**, the signal from two carbon atoms could not be observed, this is ascribed to accidental isochrony. All reagents used were reagent grade and used without further purification. The starting materials biphenyl-4-carbaldehyde, biphenyl-4,4'-biscarbaldehyde and compounds **2–4** were prepared according to procedures found in the literature. The crystals used for X-ray crystallography were obtained from HPLC grade solvents. Elemental analysis (C, H, N) was performed at DB Lab, Stenhuggervej 9, DK-5230 Odense M, Denmark. The sample was dried in a vacuum oven at 80°C for 24 h prior to the analysis.

1.1. 4,4'-Bis(1*H*-phenanthro[9,10-*d*]imidazol-2-yl)-biphenyl (**1**)

Phenanthrene-9,10-quinone (1.1 g, 5.3 mmol), ammonium bicarbonate (5 g, 63 mmol, excess) and biphenyl-

Table 1. UV–vis data for compounds **1–5** in THF



Compound	1	2	3	4	5
Concentration (μM)	23.5	13.7	24.2	64.2	46.8
λ_{max} (nm)	380	383 403	340 352 372	327 314 347 364	343
Extinction coefficient, ϵ	67262	75058 57186	42627 29946 29842	22100 21415 12219 10610	21150

4,4'-dicarbaldehyde (0.5 g, 2.4 mmol) was placed in a 100 mL conical flask containing acetic acid (50 mL). The mixture was heated to reflux forming initially a clear dark solution (initial frothing from the CO₂(g) which evolved). Reflux was continued for 1 h during which time the yellow product crystallized. After cooling overnight the product was filtered washed with acetic acid, ethanol, light petroleum and finally dried under vacuum (1.16 g, 82% yield). An analytical sample could be obtained by slow evaporation of the ethanol giving well formed yellow crystals of the bis-ethanol solvate of **1**, mp >300°C. Anal. found: C, 79.54; H, 5.79; N, 8.02. Calcd for C₄₆H₃₈N₄O₂: C, 79.53; H, 6.12; N, 7.73%. ¹H NMR (250.1 MHz, DMSO-*d*₆): δ_H 13.66 (2H, bs), 8.90 (4H, d, *J*=8 Hz), 8.65 (4H, d, *J*=8 Hz), 8.5 (4H, d, *J*=8 Hz), 8.11 (4H, d, *J*=8 Hz), 8.79 (4H, t, *J*=8 Hz), 8.68 (4H, t, *J*=8 Hz); ¹³C NMR (62.9 MHz, DMSO-*d*₆): δ_C 149.6, 140.6, 130.5, 128.5, 128.0, 127.9, 127.6, 126.2, 124.8, 122.9. *Crystal data*: C₄₆H₃₈N₄O₂, *M*=678.80, monoclinic space group *P*2₁/*c*, *a*=9.1020(18), *b*=13.147(3), *c*=14.811(3) Å; α=90, β=103.54(3), γ=90°; *V*=1723.1(6) Å³, *Z*=2, *D*_{calcd}=1.308 g cm⁻³, *T*=120(2) K, μ=0.081 cm⁻¹, *wR*₂=0.1286 (18020 reflections), *R*=0.0518 [*I*>2σ(*I*)].

1.2. 4-(1*H*-Phenanthro[9,10-*d*]imidazol-2-yl)biphenyl (**3**)

Crystal data: C₂₇H₂₀N₂O, *M*=388.45, orthorhombic space group *P*2₁2₁2₁, *a*=5.4390(11), *b*=14.143(3), *c*=24.610(5) Å; α=90, β=90, γ=90°; *V*=1893.1(7) Å³, *Z*=4, *D*_{calcd}=1.363 g cm⁻³, *T*=120(2) K, μ=0.083 cm⁻¹, *wR*₂=0.0861 (20198 reflections), *R*=0.0411 [*I*>2σ(*I*)].

1.3. (1*H*-Phenanthro[9,10-*d*]imidazol-2-yl)benzene (**4**)

Crystal data: C₂₁H₁₄N₂, *M*=294.34, monoclinic space group *P*2₁/*c*, *a*=10.282(2), *b*=15.750(3), *c*=9.2340(18) Å; α=90, β=106.26(3), γ=90°; *V*=1435.6(5) Å³, *Z*=4, *D*_{calcd}=1.362 g cm⁻³, *T*=120(2) K, μ=0.081 cm⁻¹, *wR*₂=0.2527 (13797 reflections), *R*=0.1075 [*I*>2σ(*I*)].

1.4. Crystallography methods

Crystals of **1**, **3** and **4** were drawn directly from the mother liquor, coated with a thin layer of oil, mounted on a glass capillary using grease (ApiezonTM) and transferred quickly into the cold nitrogen stream on the diffractometer. Data were collected on a Siemens SMART Platform diffractometer with a CCD area sensitive detector. Absorption corrections were made using SADABS¹⁰ Direct methods for the structure solution and full-matrix least-squares refinements were used. For compound **1** hydrogen atoms were included in calculated positions, whereas for compounds **3** and **4** the hydrogen atoms were found close to the observed positions and included in the refinements. Programs used were SMART, SAINT and SHELXTL from Siemens.^{11,12} The structures were checked for overlooked symmetry using MISSYM and for voids in PLATON.¹³ Crystallographic data (excluding structure factors) for the structures reported in this paper have

been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336033; e-mail: deposit@ccdc.cam.ac.uk] on quoting the depository numbers CCDC-156570 (**1**), CCDC-156570 (**3**), CCDC-156570 (**4**).

1.5. Photophysical methods

UV-vis spectra were recorded on a Cary 1E UV-vis spectrophotometer. The UV-vis data in THF for compounds **1–4** can be found in Table 1; data for compound **4** has been reported in ethanol and methanol.^{7,8} Fluorescence and lifetime measurements for **1** were performed on a FS900 and FLA900, respectively, from Edinburgh Instruments. The emission maximum for compound **1** was at 450 nm and the fluorescence lifetime of **1** was found to be 1.3±0.3 ns. A simple transverse optical pumping scheme¹ as shown in Fig. 1 was chosen because it did not require an elaborate laser resonator. The simple geometry does not facilitate a proper mode control, but it serves as a useful screening tool for laser dyes. In a superradiant laser system, the gain of the laser medium is so high that no resonator is required. The light emitted by the superradiant laser exhibits speckle, a sign of spatial coherence, as well as the ability to be collimated by a lens. The laser setup comprised a MiniliteTM Nd-YAG pulsed laser source from Continuum operating at a wavelength of 355 nm with a peak pulse power of 100 kW, a repetition rate of 10 Hz and a pulse width of 7 ns. The sample cell was a 1 cm fluorescence quartz cell. The cell was filled with the dye dissolved in THF (except for C120 in methanol). The concentrations of the solutions in the laser experiment were respectively for compounds **1–4** and C120: 4.5, 3.2, 18.4, 5.0 and 10.21 mM. It was irradiated with pulsed laser light focused by a cylindrical plano-convex lens with a focal length of 40 mm, as shown in Fig. 1. The laser light emitted perpendicular to the incident laser light was focused into an Oriel MultispecTM 125 diode-array¹⁴ spectrometer and the data acquisition was triggered by the laser pulses.

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