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Bartłomiej Sadowski, Marzena Kaliszewska, Guillaume Clermont, Yevgen Poronik, Mireille Blanchard-Desce, et al.. Realization of nitroaromatic chromophores with intense two-photon brightness. *Chemical Communications*, 2023, 59 (78), pp.11708-11711. 10.1039/D3CC03347C . hal-04311533

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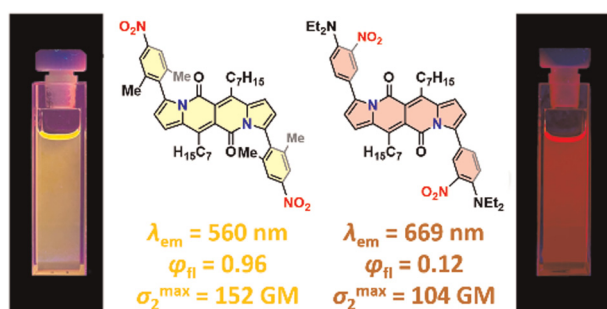
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### Realization of nitroaromatic chromophores with intense two-photon brightness

Bartłomiej Sadowski,\* Marzena Kaliszewska, Guillaume Clermont, Yevgen M. Poronik, Mireille Blanchard-Desce,\* Piotr Piątkowski\* and Daniel T. Gryko\*

Effective manipulation of electronic effects within substituted nitroaromatics based on the dipyrrolonaphthyridinedione (DPND) core leads to fluorescent dyes with enhanced emission intensity as well as two-photon response.

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# Realization of nitroaromatic chromophores with intense two-photon brightness†

Cite this: DOI: 10.1039/d3cc03347c

 Received 11th July 2023,  
 Accepted 4th September 2023

DOI: 10.1039/d3cc03347c

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**Strong fluorescence is a general feature of dipyrrolonaphthyridinediones bearing two nitrophenyl substituents. Methyl groups simultaneously being weakly electron-donating and inducing steric hindrance appear to be a key structural parameter that allows for significant emission enhancement, whereas Et<sub>2</sub>N groups cause fluorescence quenching. The magnitude of two-photon absorption increases if 4-nitrophenyl substituents are present while the contribution of Et<sub>2</sub>N groups is detrimental.**

Recent developments in molecular photonics<sup>1</sup> and biochemistry<sup>2</sup> have increased the demand for novel organic materials with improved emission characteristics and enhanced resistance towards ambient conditions. Bearing in mind the stability of  $\pi$ -conjugated organic materials, one of the most common strategies is to decrease electron density, usually enabled by introducing an electron-deficient moiety into an aromatic backbone.<sup>3</sup> The nitro group ( $-\text{NO}_2$ ) is one of the strongest electron-withdrawing moieties, and by meeting this criterion, potentially sets the stage for novel materials with intriguing optical characteristics.

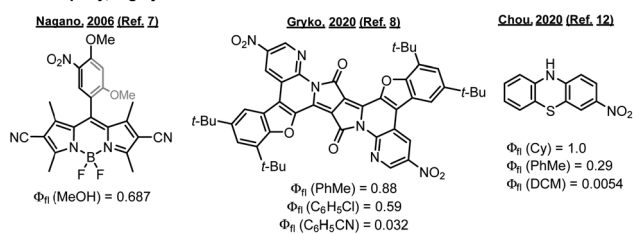
Nitroaromatics have, however, long been considered as non-fluorescent, and highly emissive examples of  $\text{NO}_2$ -containing chromophores have been sparsely reported in the literature (Fig. 1A).<sup>4</sup> Yet, they are promising candidates for constructing probes<sup>5</sup> tracking important biologically relevant species and as efficient two-photon absorbers.<sup>6</sup>

In recent years, some strategies have been developed to improve the luminescence performance of nitroaromatics.<sup>4b</sup>

From the mechanistic viewpoint, fluorescence can be successfully induced by blocking the d-PeT<sup>7</sup> process or when the nitro group does not participate in the  $S_0 \rightarrow S_1$  transition.<sup>8</sup> Applying a weaker electron-donating moiety for the construction of nitro-containing conjugates may also give rise to nitroaromatics with enhanced emission. Dyes containing nitro-functionalized thiophene,<sup>9</sup> fluorene,<sup>10</sup> tetrabenzofluorenes,<sup>11</sup> or phenothiazine<sup>12</sup> featuring enhanced emission have been described, but these approaches contain some drawbacks, such as a tendency for deexcitation *via* ISC (heavy atom effect of sulphur) or lack of significant spectral red-shifts of both the absorption and emission bands.

Due to its intriguing properties, the electron-deficient dipyrrolonaphthyridinedione (DPND) core<sup>13</sup> has recently been successfully employed in the construction of dyes with red/NIR emission,<sup>14</sup> OFETs,<sup>15</sup> stable singlet fission (SF) materials<sup>16</sup> and singlet oxygen (<sup>1</sup>O<sub>2</sub>) photosensitisers.<sup>17</sup> Studying quadrupolar, centrosymmetric DPNDs possessing two nitroaryl substituents at positions 3 and 9, we discovered that creating nitroaromatics

## A. Exemplary, highly fluorescent nitroaromatics:



## B. Nitroaryl-decorated DPNDs (this work):

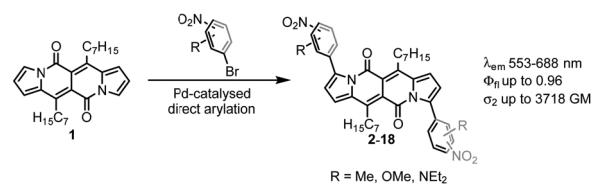


Fig. 1 Exemplary highly emissive nitroaromatics and the idea of the present work.

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† Electronic supplementary information (ESI) available: Experimental details, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra, and steady-state and time-resolved spectra. See DOI: <https://doi.org/10.1039/d3cc03347c>

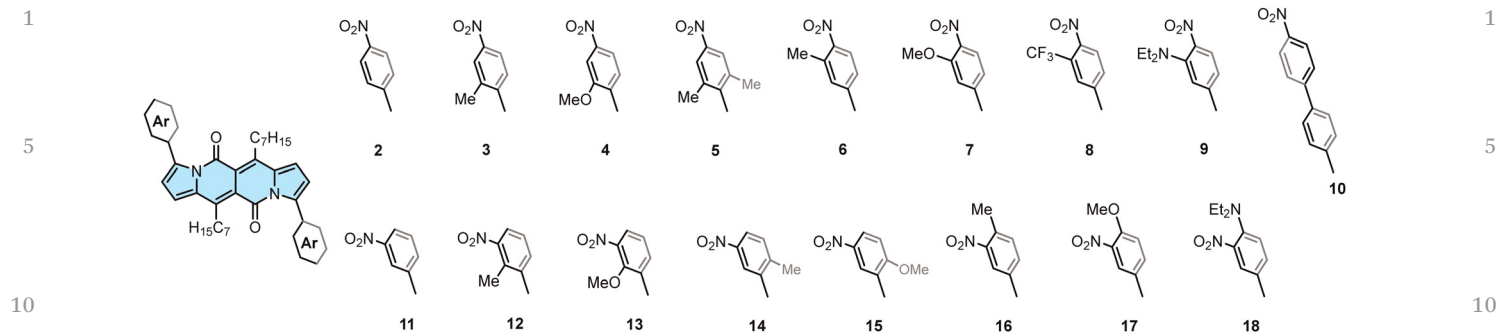


Fig. 2 Structure of nitroaromatics studied in this work.

Table 1 Comparison of spectral data for the chosen compounds in three different solvents: 1,2-dichlorobenzene (DCB), CH<sub>2</sub>Cl<sub>2</sub> (DCM), and MeCN (ACN)

Cmpd	Solvent <sup>a</sup>	$\lambda_{\text{abs}}^b/\text{nm}$	$\lambda_{\text{fl}}^b/\text{nm}$	Stokes' shift <sup>c</sup> /cm <sup>-1</sup>	$\Phi_{\text{fl}}$	$\tau^d/\text{ns}$	$k_{\text{r}}^e \times 10^{-8}/\text{s}^{-1}$	$k_{\text{nr}}^e \times 10^{-8}/\text{s}^{-1}$
<b>1<sup>f</sup></b>	DCB	508	528	750	0.81	5.1	1.59	0.373
	DCM	504	523	720	0.73	5.7	1.28	0.474
	ACN	498	525	1030	0.65	5.7	1.14	0.614
<b>2<sup>f</sup></b>	DCB	569	605	1050	0.45	3.6	1.25	1.53
	DCM	562	601	1150	0.41	3.4	1.21	1.74
	ACN	559	599	1190	0.07	—	—	—
<b>5</b>	DCB	524	560	1230	0.96	4.7	2.04	0.085
	DCM	521	560	1340	0.34	1.9	1.79	3.47
	ACN	518	564	1570	0.005	—	—	—
<b>9</b>	DCB	555	602	1390	0.006	—	—	—
	DCM	549	608	1760	0.003	—	—	—
	ACN	542	584	1330	0.003	—	—	—
<b>14</b>	DCB	525	568	1440	0.76	4.9	1.55	0.490
	DCM	522	566	1490	0.58	3.2	1.81	1.31
	ACN	520	569	1660	0.075	—	—	—
<b>18</b>	DCB	575	669	2440	0.12	2.6	0.462	3.38
	DCM	565	670	2770	0.02	—	—	—
	ACN	557	688	3420	0.04	2.8	0.143	3.43

<sup>a</sup> DCB = 1,2-dichlorobenzene; DCM = dichloromethane; ACN = acetonitrile. <sup>b</sup> Absorption and fluorescence maxima. <sup>c</sup> Stokes' shifts. <sup>d</sup> Lifetimes of the emissive excited states obtained from time-correlated single photon counting (for  $\tau \gtrsim 1.5$  ns). <sup>e</sup> Radiative and non-radiative decay rate constants:  $k_{\text{r}} = \Phi_{\text{fl}}\tau^{-1}$  and  $k_{\text{nr}} = (1 - \Phi_{\text{fl}})\tau^{-1}$ . <sup>f</sup> The data were taken from ref. 18.

with acceptor–acceptor'–acceptor (A–A'–A) architecture constitutes a new viable strategy of preventing non-radiative deactivation.<sup>18</sup>

There is, however, still a huge gap in the knowledge of how positional isomerism of the nitro group relative to the chromophore core influences the emission characteristics of nitroaromatics.

To overcome this intrinsic limitation we now report how distinct structural modifications (different substitution patterns of nitroaryl moieties) alter the emissive properties and two-photon absorption characteristics<sup>19</sup> of these quadrupolar, A–A'–A dyes.

DPNDs possessing A–A'–A architecture, considered in this work, were assembled by employing a Pd-catalysed direct arylation<sup>14b</sup> between the DPND **1** and the corresponding aryl bromides (Fig. 1, see ESI† for synthetic details). As a result, a series of new quadrupolar nitroaromatics **4–10** and **13–18** were synthesized and fully described (Fig. 2). The same method was used for the synthesis of the previously described dyes **2**, **3**, **11** and **12**, which are included here for the complete assessment of

substitution-dependent optical behaviour. The complete series of dyes differ in the location of the nitro groups (*para* or *meta*), the structure of the linker (phenyl or biphenyl), and the effect of further substitution with electron-donating or -withdrawing substituents.

The effect of structural variations on the linear optical properties of all DPND derivatives in solution was subsequently examined by employing 1,2-dichlorobenzene (DCB), CH<sub>2</sub>Cl<sub>2</sub> (DCM), or MeCN (ACN) as solvents. The results are summarized in Table 1 and Fig. S2 (ESI†), and the spectral data are shown in Fig. S1–S26 (ESI†). As expected, nitroaromatics built around the DPND core display red-shifted absorption and emission bands compared with **1**, resulting from  $\pi$ -expansion of the chromophore and the presence of groups possessing distinct electronic character.

Upon inspection of Fig. 2, two series of dyes can be recognized: **2–10** bearing nitro groups at the *para* positions relative to the DPND core, and **11–18** where the –NO<sub>2</sub> occupies *meta* positions. Regardless of the location, some trends are common to both groups. First of all, the magnitude of the response

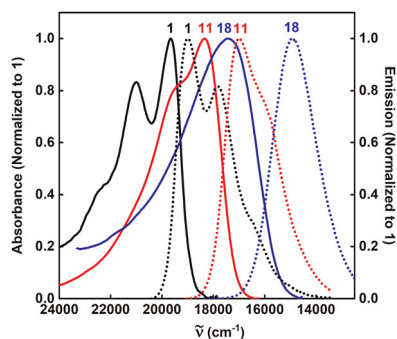


Fig. 3 Absorption and emission spectra of **1** (black solid and dotted lines), **11** (red solid and dotted lines), and **18** (blue solid and dotted lines) dyes in DCB. The **1**, **11**, and **18** emission spectra were excited at 480, 515, and 535 nm, respectively.

strongly depends on the presence of a substituent (Me, OMe) at the *ortho* position relative to the DPND core. Functionalization at this position increases the dihedral angle between the chromophore and the nitroaryl moiety, therefore decreasing conjugation, which results in a blue-shift of both the absorption and emission bands (2 vs. 3–4 and 11 vs. 12–15). Conversely, a reduced degree of rotation around the C—C single bond generally leads to an enhanced fluorescence response (Table 1 and Table S1 (ESI<sup>†</sup>), Fig. 3).

Dye 5 constitutes a special case among all the investigated nitroaromatics as it bears four *ortho*-located additional methyl groups that diminish the electronic coupling between substituents and the core, and effectively prevent the free rotation of aryl rings. This structural manipulation leads to a record-breaking value of  $\phi_{\text{fl}}$  among all nitro-DPNDs while the maxima of both  $\lambda_{\text{abs}}$  and  $\lambda_{\text{em}}$  are further hypsochromically shifted compared to those measured for 3 and 4 and just 15–30 nm bathochromically shifted vs. parent DPND 1.

The presence of an additional weak electron-donating substituent (Me or OMe) at the *ortho* position relative to the NO<sub>2</sub> group also enhances emission in all tested solvents (Table 1 and Table S1, ESI<sup>†</sup>). It marginally influences the position of both the absorption and emission bands in the case of 6 and 7 within the *para* series, while for the *meta* one, a small red-shift can be noted, especially for  $\lambda_{\text{em}}$  in 17. The potent effect of these structural factors, namely the presence of steric hindrance as well as an additional *ortho* substituent relative to the nitro group accumulates within 12, giving rise to an enormous  $\phi_{\text{fl}}$  value in relatively polar CH<sub>2</sub>Cl<sub>2</sub> (0.92).<sup>18</sup>

The incorporation of a substituent with a weak electron-accepting effect (–CF<sub>3</sub>, dye 8) or longer biaryl linkage (dye 10) does not really alter the absorption/emission characteristics as compared with 2 (Table 1 and Table S1 and Fig. S6 and S8, ESI<sup>†</sup>). At the same time, however, the presence of CF<sub>3</sub> groups leads to a sharp decrease of  $\phi_{\text{fl}}$  in polar solvents.

Finally, we investigated the influence of an auxochrome with a positive mesomeric effect (–NET<sub>2</sub>). It was found that groups featuring a strong mesomeric effect (–NO<sub>2</sub>, –NET<sub>2</sub>) placed at the *para* positions relative to the DPND core mainly govern both the absorption and emission properties of the studied DPNDs. This

Table 2 Two-photon absorption data of DPNDs 1–18 in DCM

Dye	$\lambda_{2\text{PA}}^{\text{max1}}/\text{nm}$	$\sigma_2^{\text{max1}}/\text{GM}$	$\lambda_{2\text{PA}}^{\text{max2,max3}}/\text{nm}$	$\sigma_2^{\text{max2,max3}}/\text{GM}$
1	830	27	750	44
2	820 (sh)	707	755(sh)/<690	1204/>3718
3	820	102	755/690	176/332
4	840	270	755(sh)/720(sh)	396/557
5	820	47	765/720	152/157
6	820	275	765(sh)/720(sh)	496/809
7	810	401	770/720	569/959
8	820(sh)	288	755/<690	607/>1134
9	860(sh)	0.7	755/720	4.3/5.6
10	840(sh)	319	765(sh)/720	856/1384
11	840	52	770(sh)/730	115/190
12	820	47	760(sh)/720(sh)	89/113
13	820	43	760(sh)/720	95/138
14	820	25	760(sh)/720(sh)	47/60
15	880	31	820(sh)/700	46/162
16	890	84	790/730	272/310
17	890	89	770(sh)/700	279/513
18	940	27	810/755	86/104

is particularly true for the diethylamino group in 18, giving rise to a significantly red-shifted emission (*ca.* 670 nm) but very weak fluorescence response (Fig. 3). The emission quenching is plausibly assigned to photo-induced electron transfer (PeT) occurring in the excited state.

Inspired by the large two-photon absorption (2PA) responses of nitroaromatics bearing arylolethynyl or arylolethynyl  $\pi$ -linkers between the nitro groups and the DPND core,<sup>19</sup> we investigated the 2PA properties of dyes 1–18 using the two-photon excited fluorescence (TPEF) method (see ESI<sup>†</sup>). The results are collected in Table 2 and Table S2, S3 (ESI<sup>†</sup>). No 2PA or very low response is observed in the spectral region corresponding to the lowest one-photon allowed excited state (*i.e.* above 1000 nm), due to symmetry reasons.<sup>20</sup> In contrast, significant 2PA broad bands (or shouldering) in the 800–850 nm range and even more intense 2PA bands closer to 700 nm are observed at higher energy (Fig. 4). The 2PA magnitude in the NIR1 region strongly depends on the structure of the dyes and the nature and position of the substituents (Table 2). The presence of NO<sub>2</sub> substituents at the *para* position is a key structural factor: analogous dyes from the *meta* series show much smaller 2PA responses, as noted from the comparison of dyes 2 and 1; 3 and 12; and 4 and 13 (Fig. S27, ESI<sup>†</sup>). For the derivatives having a

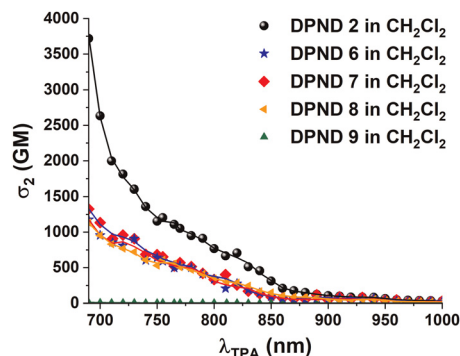


Fig. 4 Two-photon absorption spectrum of DPND 2, 6–9 in CH<sub>2</sub>Cl<sub>2</sub>.



1 *para* NO<sub>2</sub> group (2–10), the presence of an additional substituent generates a marked decrease of the 2PA both in the case of substituents positioned in the *ortho* (Fig. 4) or *meta* (Fig. S28, ESI<sup>†</sup>) position. For the derivatives having a *meta* NO<sub>2</sub> group (11–18), the influence of additional substituents is different depending on their position (Fig. S28, ESI<sup>†</sup>). Indeed, the presence of electron-donating MeO in the *para* position leads to a larger 2PA response compared to derivative 11. We yet note that DPNDs 9 and 18 possessing Et<sub>2</sub>N substituents have markedly weaker two-photon absorption (Fig. 4 and Fig. S3, ESI<sup>†</sup>) most probably due to steric hindrance. Finally, adding an additional 1,4-phenylene moiety in *para* NO<sub>2</sub> derivatives does not lead to an increase of the 2PA (Table 2 and Fig. S29, ESI<sup>†</sup>), indicating that the biphenyl twist may prevent extended delocalization favorable to 2PA enhancement.

To conclude, we found that strong fluorescence is a general feature in quadrupolar, centrosymmetric dipyrrolonaphthyridinediones possessing nitrophenyl substituents. Two-photon allowed transition to higher excited states is responsible for the main two-photon absorption band located around 700 nm. Combining the steric and electronic effect of various substituents enables the fine-tuning of both one-photon and two-photon absorption reaching emission at *ca.* 670 nm and a strong 2PA response (two-photon brightness > 1500 GM). Careful selection of the substitution pattern allows for effective control of the optical response, which builds the foundation for designing efficient one- or two-photon absorbers based on other cross-conjugated chromophores.

Conceptualization: B. S.; investigation: B. S., G. C., M. K., P. P.; supervision: D. T. G., M. B.-D., P. P.; visualization: B. S., Y. M. P.; writing – original draft: B. S, D. T. G.; writing – review & editing: D. T. G., M. B. D, B. S.

The work was financially supported by the Polish National Science Centre, Poland (Sonata 2021/43/D/ST4/02267) and the Foundation for Polish Science (TEAM POIR.04.04.00-00-3CF4/16-00).

## Conflicts of interest

There are no conflicts to declare.

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