

An Efficient Microwave-assisted Synthesis of Sonogashiracoupled PMI Derivatives: Impact of Electron Donating Groups on Optoelectronic Properties

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Abstract: An efficient microwave-assisted Sonogashira-coupling protocol for *peri*-functionalised perylenemonoimide dye derivative is presented. This method is significantly faster than conventional coupling method providing a moderate to good yield and interesting optoelectronic properties. The electronic communication between electron-rich aryl and poly aryl groups with the perylene core *via* C=C bonds is investigated.

Rylene dyes such as perylenemonoimide (PMI), perylene bisimides (PDI), terylenemonoimides (TMI), Terylene di-imides (TDI) have found wide spread applications ranging from industrial pigments to components of molecular photonic devices.^[1] PMI dyes have drawn attention due to their unique properties such as high fluorescence quantum yield,^[2] high stability^[3] and implemented as a suitable candidate for energy transfer, photocatalysis and nonfullerene-based organic solarcells.^[4] The synthetic chemistry of PMI dyes has developed rapidly over the past few decades, by converting commercially available perylene-3,4,9,10-tetracarboxylic dianhydride into PMI.^[3]

The primary challenge in working with perylene dyes is associated with their intrinsic low solubility. Lately, 2,5-ditertbutyl, 2,6-diisopropyl phenyl groups, or alkyl groups were incorporated at the N-atom of the imides moiety to tackle the solubility problem without affecting the optical properties.^[1b, 4b, 5] Variation of their imide substitution can influence the solid-state packing but impart a negligible effect on solution properties because of the nodes present at the imide nitrogen.[1b, 4b, 5] The bay and peri position of PMI A was functionalized to achieve further solubility (Figure 1) as well as a change in the optical properties.^[5b, c, 6] Müllen ^[5c, 6] and Lindsey ^[4a, 5b, 7] have developed methods for the halogenations at bay and peri-position of PMI and subsequent substitution of the halogenated PMI dyes. Literature studies^[7] show that functional groups at the node of PMI have no effect on its optical properties, but that the presence of an OAr group at the peri position [PMI(OAr) B, Fig. 1] shifts the absorption maximum (λ_{abs}^{max}) to a longer wavelength, compared to unsubstituted PMI A.^[7] However, by introducing one OAr shows a shift of 26 nm in toluene where as three OAr groups at bay and peri position (1, 6, and 9- position) of the PMI [PMI(OAr)₃ C, Fig. 1] the λ_{abs}^{max} is shifted by 30 nm, suggesting a small change due to the bay functionalization.^[1a, 8] Similarly, when the bay region of the fluorophore D is replaced with an electron withdrawing CN groups λ_{abs}^{max} of the resulting fluorophore E

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shows only 7 nm red shift, further supports the small effects due to bay functionalization (C-1 and C-6).^[9]



Figure 1 Structural representation of different PMI dyes derivatives containing functional group at bay and *peri* position

Tomizaki et al.^[7] reported the functionalized PMI F where the peri position was substituted by pyrrolidino group and the bay positions were with the OAr groups (**F**, Fig. 1). The λ_{abs}^{max} shows a red shift of 95 nm in comparison to PMI A and 65 nm in comparison to the fluorophore **C**. Such a large shift in the λ_{abs}^{max} is due to the conjugation of electron pair on the N-atom of the pyrrolidino group with PMI core. Considering a dramatic change upon peri-functionalization of PMI, we came to the hypothesis that introduction of π -conjugation may extend electronic communication further leading to interesting optical properties. As part of our continuing studies on the optoelectronic properties of PMI derivatives, we employed the standard Sonogashiracoupling methods (reaction time 18 h) to synthesize the PMI derivatives.[5a, b] We introduced microwave-assisted Sonogashira-coupling reaction keeping in mind its increasing interest for reduced reaction times.^[10] Despite these benefits, microwave-assisted synthesis remains underutilized for the chemical manipulation of rylene dyes.[10d, 11]

Herein, we report a microwave-assisted synthesis of 9-bromo PMI **2**, a library of Sonogashira-coupled *peri*-functionalized PMI derivatives **3**, and **6a-i**, (Scheme 1) and alkynyl coupled electron-rich aryl and poly aryl compounds **8c-g** precursor for **7c-g** (see SI) at reaction rates significantly faster than the conventional method. The optoelectronic properties of the synthesized *peri*-functionalized PMIs **6a-i** were extensively studied and compared with PMI derivative **6'** (see Figure 1) prepared *via* Suzuki coupling.^[12]

With an aim toward the rapid synthesis of perylene derivatives with novel properties, we performed bromination at the *peri*position of PMI by refluxing PMI **1** with Br₂ in DCM for 2-3 h to obtain the 9-bromo PMI **2** in 80-90 % yield.^[4f, 5b, 13] Interestingly, the bromination reaction was carried out in DCM at 40 °C for 5 minutes by using microwave-assisted irradiation and 9-bromo PMI **2** was isolated in 90% yield. The brominated product **2** was coupled with the TIPS acetylene in a microwave reactor at 75 °C

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for 25 min against the traditional procedure. The TIPS group of THF) at room temperature for 20 min to obtain the 9-ethyne PMI **4** in 80-90 % yields. The 9-arylakynyl-coupled PMI **6** can be synthesized by two possible routes *via* (A) by coupling the 9-

the PMI derivative **3** was further treated with TBAF (1.0 M in ethyne PMI **4** with aryl halides **5**, (B) by coupling PMI-Br **2** with the different arylalkynes **7** (scheme 1).



a) Br₂, DCM, 40 °C, 5 min, μ -wave; b) TIPS acetylene, Pd₂(dba)₃, P(o-tolyl)₃, toluene, Et₃N, 75 °C, 25 min, μ -wave; c) nBu₄NF, THF, rt, 20 min; d) Pd₂(dba)₃, P(o-tolyl)₃, toluene, Et₃N, 40-55 °C, 5-10 min, μ -wave (synthesis of compound **6a-e**); PdCl₂(PPh₃)₂, Cul, THF, piperidine, 40 °C, 5 min, μ -wave (for compounds **6f-i**); e) Pd₂(dba)₃, P(o-tolyl)₃, toluene, Et₃N, 65 °C, 18 h (synthesis of compounds **6a-e**), PdCl₂(PPh₃)₂, Cul, THF, piperidine, rt, 18 h (for **6f-i**); f) Pd₂(dba)₃, P(o-tolyl)₃, toluene, Et₃N, 55 °C, 5-10 min, μ -wave (compounds **6a-e**)

Scheme 1 Synthesis details of the peri-functionalized PMI derivatives

We have carried out the synthesis of compound **6** by following the route **A** using the Sonogashira coupling by traditional as well as microwave-assisted irradiation. By using the microwaveassisted protocol, the compounds **6a-i** were synthesized with a comparable yield with the traditional route and the reaction time was dramatically reduced from 18 h to 5-10 min (scheme 1). By following the route B, *peri*-functionalized PMI derivatives **6a-6g** were synthesized by using the microwave-assisted protocol with good to excellent yield and it seems to be an efficient route (scheme 1, table 1).

 Table 1 Reaction temperature, duration and % of yields for the synthesis of PMI derivatives 6a-i

PMI	Route A	Route B					
	Traditional	MW assisted			MW assisted		
_	yield ^{a,b}	T /°C	t /min	yield ^a	T /°C	t /min	yield ^a
6a	42	55	10	31	55	5	83
6b	59	55	10	76	55	5	87
6c	49	55	10	43	55	10	65
6d	69	40	5	71	40	10	73
6e	40	40	5	73	40	10	73
6f	60	40	5	64	40	10	69
6g°	46	40	5	52	40	10	68
6h	65	40	5	86	-	-	-
6i [°]	70	40	5	85	-	-	-

^aIsolated yield (%); ^bFor route A, conventional synthesis, the reaction temperature was 65 °C, in toluene/TEA and reaction time was 18 h; ^cEven after several attempts the coupling partner free acetylene **7h & 7i** were not isolated.



Figure 2. Absorption spectra of (a) 1, 6', 6a; and (b) 1 with representative PMI derivatives in toluene

The compounds 6h and 6i were not synthesized by route B as we failed to isolate the free acetylene 7h and 7i in several attempts due to their low-boiling point. The synthesis of free acetylenes 7c-g was reported in the SI. The library of different peri-functionalized PMI derivatives 6a-i showed good solubility in common organic solvents such as DCM, chloroform, THF and toluene. However, the synthesized molecules are sparingly soluble in polar aprotic solvents such as DMF and DMSO. Our objective is to see the effect of the extension of PMI core along the long molecular axis (specifically at 9-position of PMI), which enables a systematic comparison of their optical properties. All UV-Vis. solvent dependent absorption, steady-state fluorescence, and time-resolved fluorescence measurements were performed at room temperature (298 K). Irrespective of the

solvent polarity, the λ_{abs}^{max} of the peri-functionalized PMI derivatives 6a-i have a significant shift (ca. 25 nm for 6i and 49 nm in case of 6c) as compared to the parent PMI 1. In toluene, 1 has two major absorption peaks one at 477 nm and other at ca. 504 nm. It indicates, that there is noteworthy variation in the vibrational energy of the excited PMI derivatives upon substitution. However, when it was coupled at the peri position, it was bathochromically shifted with different extent. In compound 6a, tolyl group is present at the peri position of PMI, leading the λ_{abs}^{max} bathochromically shifted by 31 nm in case of **1** in toluene. It is fair enough to compare the parent PMI 1, the Suzuki-coupled PMI 6' with the π -extended sonogashira-coupled PMI 6a as the methyl group on the tolyl phenyl has a negligible electronic effect (Figure 2(a) and Table 2). To verify, we have performed DFT calculations to find out the HOMO-LUMO energy of selected PMI derivatives (Fig. S55 and Table S2) and the electron density and matches well with the values obtained for similar molecules.^[14] The λ_{abs}^{max} of **6'** bathocromically shifted by 11 nm in comparison to 1 in toluene, whereas the λ_{abs}^{max} of **6a** is bathochromically shifted by 20 nm with respect to 6', showing the effect of C≡C spacer in the ground state along the long axis of the pervlene.

There is a minor spectral shift of 2 nm and 5 nm in λ_{abs}^{max} in the case of **6c** and **6g** respectively, with respect to **6a** (Table 2 and S1). However, in case of polar solvent DMF the λ_{abs}^{max} of **6c** and **6g** are bathochromically shifted 10 to 20 nm with respect to **6a** (Table S1). The steady-state fluorescence measurement of PMI **1**, **6'**, and **6a** in toluene shows that emission maxima (λ_{em}^{max}) of **6'** is bathochromically shifted by 19 nm with respect to **1**, and for **6a** it was bathochromically shifted by 10 nm in comparison to **6'** (Figure 3).



Figure 3. Normalized emission spectra of (a) 1, 6', 6a; and (b) 1 with some representative PMI derivative in toluene

The λ_{em}^{max} of *peri*-coupled PMI derivatives **6a-i** are redshifted by 29-109 nm in toluene with respect to PMI **1** (Table 2). For electron-rich functional derivatives *i.e.*, **6c** and **6g**, the λ_{em}^{max} red-shifted by 109 nm and 94 nm respectively. The quantum yield of the compounds **6a-i** is quite high except **6c** (0.62) and **6d** (0.50) in toluene (Table 2). In polar solvents, ϕ_f of **6c** and **6g** are quite low (see SI) due to strong dipolar interactions with solvents. The timeresolved measurements of **6a-i** show the lifetime spanning from 1.5 ns to 3.9 ns in dichloromethane. However, we did not observe any significant changes in fluorescence lifetime with solvent polarity (see Table S1) except in case of **6g**. Akin to UV-Vis. properties, not much alternation in the first 1e reduction potential value was observed upon substitution at *peri* position as can be seen from the electrochemical measurements. Interestingly, the potential values are very similar to the *peri*-functionalized Suzuki-couple product **6'**. Reductions of PMI derivatives were reversible in nature although in case of oxidation for **6c**, **6g**, **6h** and **6i** quasi-reversible or irreversible peak was observed. Mostly, one electron oxidation seems much more favourable compared to unsubstituted PMI except in case of **6a**. Interestingly, a notable variation of *ca*. 0.15 V was measured in case of second 1e reduction potential, which is much more difficult compared to first reduction due to substitution at *peri* position and indicating stabilization due to increased conjugation.

Table 2 Optical and electrochemical properties of PMI 1, 6', and $\it peri-coupled$ PMI derivatives $6a-i^a$

PMI	$\varepsilon x 10^4 / M^{-1} cm^{-1}, (\lambda_{abs}^{max} / nm)$	λ _{em} ax /nm	Φ_{f}^{b}	τ _{avg} /ns	E _r (1) /V	E _r (2) /V	E₀(1) /V
1	4.0, (504)	526	0.48	4.7	_	1.20	1.08
6'	4.0, (515)	545	0.99	4.4	0.95	1.42	1.35
6a	4.7, (535)	555	0.81	3.5	0.95	1.35	1.35
6b	4.3, (535)	565	0.79	3.5	0.95	1.27	1.26
6c	4.1, (537)	635	0.62	3.0	0.95	1.25	0.90 ^c
6d	3.4, (530)	560	0.50	3.4	0.90	1.22	1.27
6e	4.8, (536)	560	0.84	3.2	0.93	1.20	1.18 [°]
6f	5.4, (536)	560	0.84	3.3	0.90	1.20	1.26
6g	4.6, (540)	620	0.87	3.0	0.95	1.30	0.95 ^d
6h	5.5, (533)	560	0.88	3.5	0.91	1.26	e
6i	5.2, (530)	555	0.98	3.7	0.91	1.26	e

^aOptical and electrochemical properties are measured in toluene and dichloromethane respectively; the half-wave potential $E_{r/o}$ was set equal to 0.5 ($E_{pa} + E_{pc}$), where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively. ^b Φ_{f} was measured with reported reference compound 2,6-Diisopropylaniline substituted PMI in toluene.^[7] csplit observed in cathodic CV peak. ^doxidation was irreversible. ^eno distinct peak was observed.

In conclusion, we have developed a simple microwave-assisted synthetic protocol for a series of *peri*-coupled PMI derivatives by Sonogashira coupling at reaction rates that are significantly faster than conventional techniques with high reaction yield can be utilized for other dyes and polymer chemistry. These molecules display high molar extinction coefficient, near-unity fluorescence quantum yield, substitution-dependent optoelectronic properties, and electrochemical properties with a real promise for different applications. Currently, we are exploring their potential in fluorescent materials and solar-cell applications.

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