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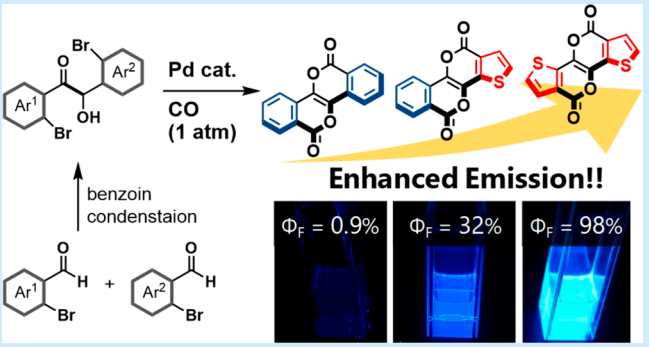
Palladium-Catalyzed Double Carbonylative Cyclization of Benzoins: Synthesis and Photoluminescence of Bis-Ester-Bridged Stilbenes

Yosuke Tani* and Takuji Ogawa*

Department of Chemistry, Graduate School of Science, Osaka University, Machikaneyama 1-1, Toyonaka, Osaka 560-0043, Japan

Supporting Information

ABSTRACT: A palladium-catalyzed double carbonylative cyclization of benzoins has been developed, which realizes the synthesis of bis-ester-bridged stilbenes just in two steps from aldehydes. Thus, the obtained fully fused tetracyclic π-systems have a pyrano[3,2-*b*]pyran-2,6-dione (PPD) core on their center, showing two reversible reductions at low potentials. In addition, their photoluminescence properties are strikingly affected by the aromatic rings fused to the PPD core; bis-*thieno*-fused PPDs are found to be excellent fluorophores with quantum yields up to 0.98.



Polycyclic fused π-conjugated systems such as bridged stilbenes, triphenylenes, and acenes are a privileged motif in optical and electronic materials, including organic light-emitting diodes and organic photovoltaics.[1] Therefore, efficient synthetic strategies for such fused skeletons are of great interest.[2] Many of the established routes construct them from preorganized, nonfused π-systems (Figure 1a), e.g. from oligoarenes by Scholl reaction or direct arylation,[3] or from functionalized diaryl acetylenes into bridged stilbenes.[4] In this context, benzoins can be a promising precursor for fused π-systems, since they are available directly from aldehydes by benzoin condensation and have a stilbene skeleton in the enol form (Figure 1b). The development of a suitable transformation of benzoins will expand the chemistry of bridged stilbenes that are otherwise difficult to access. In particular, bis-ester-bridged stilbenes (Y is C═O in Figure 1b) are attractive because the ester group is electron-withdrawing, chemically convertible, and redox active, and it composes a weakly aromatic 2-pyrone substructure.[5,6] Interestingly, they are also found in some natural products.[7] Nonetheless, the synthesis and properties of bis-ester-bridged stilbenes are virtually unexplored.[8]

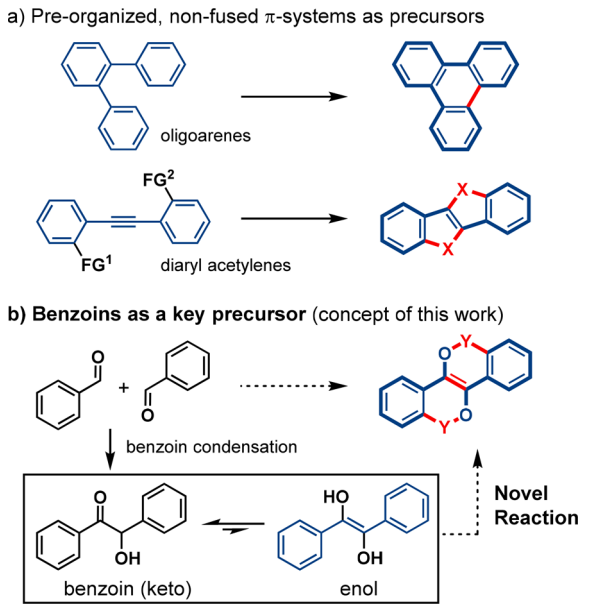


Figure 1. Synthetic strategy toward polycyclic fused π-systems utilizing (a) preorganized π-systems and (b) benzoins as an easily available, latent π-system (This work). FG = functional group.

We envisioned that Pd-catalyzed carbonylation chemistry[9] would offer a powerful solution for the conversion of benzoins into bis-ester-bridged stilbenes. In particular, carbonylative cyclization has been utilized in the synthesis of heterocycles,[10] although the construction of multiple rings is rarely achieved.[11] Herein, we have developed a palladium-catalyzed double carbonylative cyclization of benzoins, which affords bis-ester-bridged stilbenes having a pyrano[3,2-*b*]pyran-2,6-dione (PPD) core on its center. The reaction reveals a stilbene skeleton, fixes the planar π-system, and installs electron-withdrawing functionality at one time, thus providing them with unique electronic and photophysical properties.

We began by benzoin condensation of 2-bromoarylaldehydes **1a**−**1e**, which are readily available by several approaches (Scheme S1 in the Supporting Information (SI)).[12] After the corresponding benzoins **2a**−**2e** were successfully synthesized, double carbonylative cyclization of **2e** was examined under various conditions (Table 1). The reaction mainly produced

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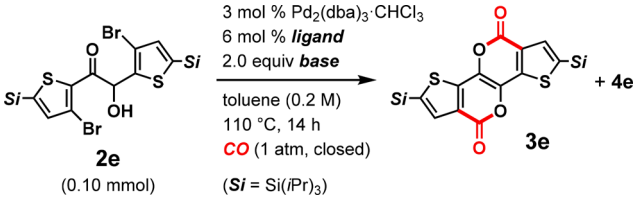
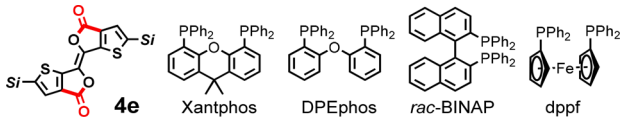
Table 1. Pd-Catalyzed Double Carbonylative Cyclization of 2e



entry	ligand	base	yield (%)[a]	3e/4e[b]
1	Xantphos	Cs_2CO_3	42	>95/5
2	Xantphos	CsOAc	88	85/15
3	**Xantphos**	**KOAc**	**95**	**87/13**
4	Xantphos	NaOAc	49	>95/5
5	DPEphos	KOAc	65	60/40
6[c]	dppf	KOAc	52	42/58
7	*rac*-BINAP	KOAc	20	25/75
8[d]	Xantphos	KOAc	76	88/12
9[d]	Xantphos	KOAc[e]	92	85/15

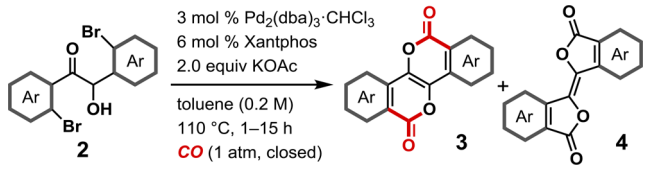
[a]Combined yields of **3e** and **4e** determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b]Determined by ^{1}H NMR. [c]$PdCl_2$(dppf) (6 mol %) was used as the catalyst. [d]$PdCl_2(PhCN)_2$ (6 mol %) was used instead of $Pd_2(dba)_3$·$CHCl_3$. [e]KOAc (3.0 equiv) was used.

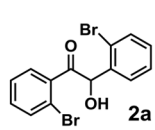
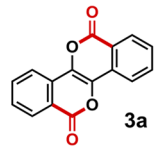
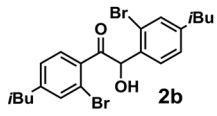
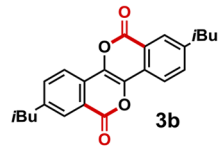
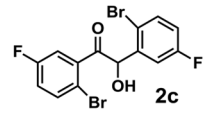
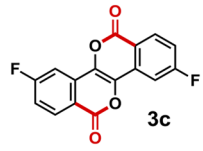
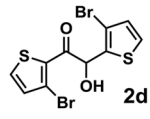
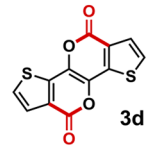
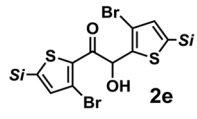
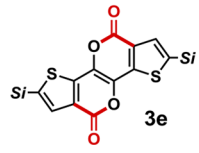


fully fused target **3e** and its structural isomer **4e**, and was quantitatively evaluated by ^{1}H NMR using an internal standard. First, we tested the effect of a base by using $Pd_2(dba)_3$·$CHCl_3$ as a catalyst precursor and Xantphos as a ligand[9b] under 1 atm of carbon monoxide (CO) in toluene at 110 °C (entries 1–4). When we used Cs_2CO_3, **3e** was obtained in 42% yield (entry 1), which was the highest among other tested carbonate bases and KO*t*Bu. These strong bases were expected to facilitate enolate formation.[10b] However, weakly basic acetates were found to be far more effective for this transformation, possibly due to the easily enolizable nature of benzoins. Using CsOAc, **3e** was obtained in 75% yield along with a non-PPD structural isomer **4e** (13%, entry 2).[13] The best yield for **3e** was achieved by employing KOAc; the combined yield of **3e** and **4e** reached 95%, and the ratio was 87/13 (entry 3). Although the selectivity was improved with NaOAc, the total yield dropped to 49% (entry 4). The choice of ligand was also crucial. Other bidentate phosphines DPEphos, dppf, and *rac*-BINAP were not as effective as Xantphos was; the total yields decreased to 65%, 52%, and 20%, respectively (entries 5–7). The selectivity (isomer ratio) was much affected, even reversed in the case of dppf and *rac*-BINAP, implying that the catalyst is involved in the selectivity-determining step (see SI for further discussion). As for a catalyst precursor, a divalent palladium source, $PdCl_2(PhCN)_2$ complex, led to a slight decrease in the yield while maintaining the selectivity, suggesting that the palladium complexes enter the catalytic cycle as Pd(0) species (entry 7). The yield was restored by increasing the amount of KOAc to 3 equiv (entry 8).

With the optimized conditions in hand, we completed the synthesis of fused PPDs by the double carbonylative cyclization of benzoins **2a**–**2e** (Table 2). The conditions were demonstrated to be effective not only for thiophene-derived benzoins but also for benzene-derived benzoins. For example, **2a** was

Table 2. Synthesis of Fused PPDs 3a–3e from Benzoins 2a–2e[a]



entry	benzoin **2**	fused PPD **3**	isolated yield **3** (%)	**4** (%)
1	 **2a**	 **3a**	81	6
2			64[b]	8[b]
3	 **2b**	 **3b**	66	13
4[c]	 **2c**	 **3c**	65	6
5	 **2d**	 **3d**	25	—
6	 **2e**	 **3e**	72	6

[a]Conditions: **2** (0.20 or 0.10 mmol), $Pd_2(dba)_3$·$CHCl_3$ (3 mol %), Xantphos (6 mol %), KOAc (2.0 equiv) in toluene (0.2 M) under CO (1 atm, closed) at 110 °C. [b]On 1.0 mmol scale. [c]At 90 °C. *Si* = triisopropylsilyl.

efficiently converted to **3a** and **4a** in a ratio of 90/10 as judged from ^{1}H NMR of the crude mixture. Product **3a** was isolated in 81% yield after silica-gel column chromatography (entry 1). The same reaction was also performed in 1.0 mmol scale, affording 170 mg of **3a** (entry 2). The syntheses of fused PPDs **3b**, **3c**, and **3e** having alkyl chain, fluorine, and silyl substituents, respectively, were also examined because these substituents are often utilized to control crystal packing.[1a,b,f,14] As a result, those fused PPDs were successfully synthesized and isolated in good yields (65–72%). Thieno-fused PPD without any substituents (**3d**) was obtained, albeit in low yield, partly owing to its limited solubility.

We further extended the strategy to the synthesis of unsymmetrically fused PPDs. Benzoin **2f** was prepared by cyanosilylation of **1a** followed by deprotonation with lithium diisopropylamide and trapping with **1e** (see Supporting Information (SI) for detail). Double carbonylative cyclization of **2f** proceeded efficiently under the standard conditions, affording *benzo-thieno*-fused PPD **3f** in 72% isolated yield (eq 1).

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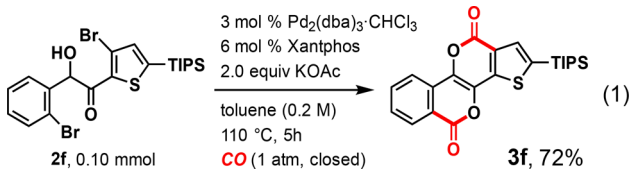

All the structures of fused PPDs **3a**–**3f** were unambiguously determined by single-crystal X-ray structure analysis (Figure 2

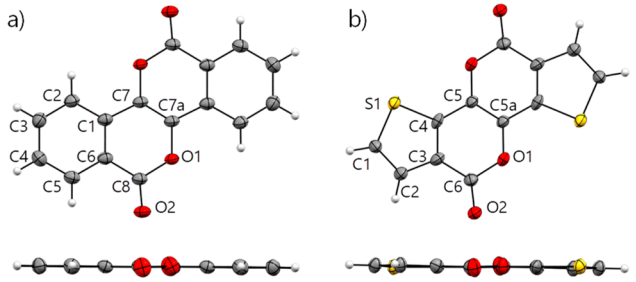

Figure 2. ORTEP drawing of the crystal structures for **3a** (a) and **3d** (b). Thermal ellipsoids are set at the 50% probability level. Selected bond lengths for **3a**: C1–C7, 1.437(2); C7–C7a, 1.341(2) Å. For **3d**: C4–C5, 1.435(7); C5–C5a, 1.343(6) Å.

for **3a** and **3d**; see SI for others). Except **3f** whose skeleton was slightly bent in the crystal, all the other fused PPDs had planar skeletons. All, except **3e**, were packed very tightly (interplanar distances of the parallel stacked pairs: 3.17–3.39 Å) with various short contacts including hydrogen bonding on the carbonyl oxygen. Moreover, their packing modes can be tuned by substituents and the skeleton: herringbone stacking for **3a** and **3c**, brick wall 2D stacking for **3b**, 1D columnar stacking for **3d**, and antiparallel pairwise 1D stacking for **3f**. We also performed thermogravimetric analysis of **3a** and **3d**, which did not show any indication of decomposition (Figure S1). Temperatures for 5% weight loss were at 275 and 317 °C, respectively, both of which corresponding to sublimation of the compounds. As for the electrochemical property, cyclic voltammograms of **3b** and **3e** in tetrahydrofuran were measured. They showed two reversible reduction peaks at −2.71 and −2.31 V for **3b** and −2.37 and −1.91 V for **3e** (versus Fc/Fc^+), which demonstrated their electrochemical stability and low lying LUMO (−2.5 eV for **3b** and −2.9 eV for **3e**, Figures S2 and S3).[5,6] These thermal and electrical properties as well as tunable molecular arrangements in crystal indicate that fused PPDs are promising materials for the application in organic electronics.

UV–vis absorption and photoluminescence (PL) spectra as well as photoluminescence quantum yields (Φ_F)[15] of fused PPDs were measured in degassed dichloromethane (Figure 3 and Table 3 for representative data; see SI for full details). For all fused PPDs **3a**–**3f**, UV–vis and PL spectra are mirror images of each other with vibrational structure, and the Stokes shifts are very small. These features imply their rigidness and structural similarity in the ground state (S0) and the first singlet excited state (S1). More specifically, along with replacing the peripheral fused ring from benzene to thiophene (i.e., **3a** → **3f** → **3e**, from bottom to top in Figure 3), the vibrational structure became sharper with progression of 0–0 band, and the Stokes shifts became smaller (11 nm for **3a**, 9 nm for **3f**, and 4 nm for **3e**). These trends clearly indicate that the structural displacement in S1 becomes much smaller in this order. In addition, both UV–vis and PL spectra are bathochromically shifted about 40 nm in

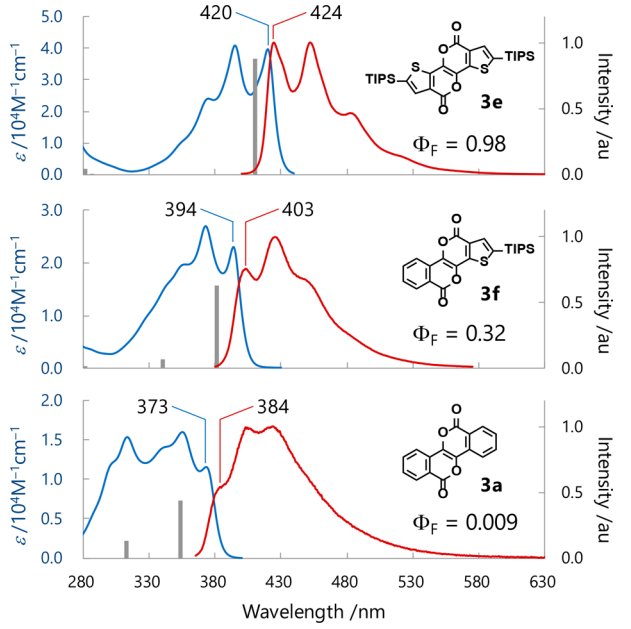

Figure 3. UV–vis absorption (blue) and normalized PL (red) spectra for **3e** (top), **3f** (middle), and **3a** (bottom) in CH_2Cl_2. Oscillator strengths of absorption (TD-DFT//B3LYP/6-31+G**) are depicted as gray bars. Φ_F are relative to quinine sulfate.[15] Left axis for UV–vis, right axis for others.

Table 3. Photophysical Properties of 3a–3f and 4e

compd	λ_{abs} (nm)[a]	ε (M^{-1} cm^{-1})[b]	λ_{em} (nm)[c]	Φ_F[d]	k_r (ns^{-1})[e]	k_{nr} (ns^{-1})[e]
3a	373	16 000	384	0.009	0.29[f]	32[f]
3b	382	19 600	395	0.049	n.d.	n.d.
3c	364	18 100	370	0.004	n.d.	n.d.
3f	394	26 900	403	0.32	0.37	0.79
3d	408	33 700	413	0.90	0.38	0.042
3e	420	40 800	424	0.98	0.38	0.0078
4e	419	45 900	427	0.31	0.41	0.92

[a]The longest absorption maxima. [b]At the global maxima. [c]The shortest emission maxima. [d]Determined relative to quinine sulfate.[15] [e]Calculated with Φ_F and τ according to the formula $k_r = \Phi_F/\tau$ and $k_{nr} = (1 - \Phi_F)/\tau$. [f]Calculated with λ_{em}, oscillator strength, and Φ_F. See Table S2 in SI for detail. n.d. = not determined.

total, suggesting that thieno-fused systems have a smaller HOMO–LUMO gap and more delocalized π-system than benzo-fused ones do. Indeed, according to time-dependent density functional theory (TD-DFT) calculation at the B3LYP/6-31+G(d,p) level of theory, the strongest transitions in **3a**, **3f**, and **3e** are of S0–S1 (HOMO–LUMO 94% or more) and are essentially a π–π^* transition in nature, for both absorption and emission.

The peripheral aromatic rings most substantially effected Φ_F. *Thieno*-fused PPDs **3d** and **3e** exhibited much higher Φ_F (≥0.9) than *benzo*-fused PPDs **3a**–**3c** did (Φ_F < 0.1). The highest Φ_F was observed for **3e** (0.98) while **3d** still showed a high Φ_F of 0.90, suggesting that the highly fluorescent nature is attributed to the core skeleton itself, rather than to the silyl substituent.[16] This is also evident from a comparison of **3e** and its structural isomer **4e**. Their UV/PL spectra were similar in peak positions and molar extinction coefficient (ε); however, **4e** showed somewhat broadened spectra (Figure S4), as well as a much diminished quantum yield of 0.31. This emphasizes the

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superiority of the PPD core for the structural rigidity even in the excited states.

We further evaluated the radiative and nonradiative decay rate constants (k_r and k_{nr}) of **3a**, **3d**−**3f**, and **4e** (Table 3; see SI for details). According to the equation $\Phi_F = k_r/(k_r + k_{nr})$, it is clearly revealed that the strong dependency of Φ_F on their fused aromatics originates from a difference in k_{nr}, which is 4 orders of magnitude for **3a** to **3e**. In addition, **4e** exhibits a 2-order larger k_{nr} than that of **3e**. These trends in the rate constants again prove the structural rigidity, or more specifically, the sharpness of potential energy surface[17] of fused PPDs especially for thieno-fused ones. It should be noted that k_{nr} includes intersystem crossing. Nonetheless, a negligible decrease of PL intensity was observed under air-saturated condition. Moreover, the PL spectrum of **3a** measured at 77 K in 2-methyltetrahydrofurane displayed imperceptible phosphorescence (Figure S6). Thus, the intersystem crossing is sufficiently slower than the radiative S1−S0 decay and can be ignored in the photophysical process.

In summary, we have developed a novel Pd-catalyzed double carbonylative cyclization of benzoins, and established the versatile synthesis of bis-ester-bridged stilbenes in two steps from aldehydes. They exhibited unique thermal and electrical properties as well as tunable crystal packing, owing to the carbonyl functionality. Moreover, their photophysical properties unexpectedly depend on the peripheral aromatic rings fused to the PPD core, and bis-thieno-fused PPDs are demonstrated to be a novel class of excellent fluorophores. Further studies to exploit the potential of the fused PPDs are ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03169.

Experimental procedures, characterization of new compounds, physicochemical properties, and theoretical calculations (PDF)

Accession Codes

CCDC 1858128−1858129 and 1859329−1859333 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: y-tani@chem.sci.osaka-u.ac.jp.
*E-mail: ogawa@chem.sci.osaka-u.ac.jp.

ORCID

Yosuke Tani: 0000-0003-1326-5457

Notes

The authors declare no competing financial interest.

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