Electronic Supporting Information

Solid-State Fluorescence of A Quasi-Isostructural Polymorphic Biphenyl Based Michael Addition Product

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Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) of the as synthesized Form 1 (compound **A**) shows single melting endotherm (onset 163 °C) without any possible phase transformation. The additional broad endotherm around 60 °C may be due to a small amount of PEG present during isolation of the compound and further confirmed using solution ¹H NMR analysis (see ESI Figure S3). On the other hand the powder sample containing polymorphic mixture (Form 1 and 2) obtained from solution crystallization from 1:1 mixture of n-Hexane and THF shows a small phase transition (onset 104 °C) prior to melting which may be due to conversion of Form 2 to Form 1 followed by melting at 169 °C (melting onset) (Figure S1). Thermal analysis suggested Form 1 monotropically related to Form 2; whereas Form 2 converts to Form 1 under high temperature (enantiotropic).



Figure S1 DSC thermogram of (a) compound **A** pure Form 1 (red line) and mixture containing Form 1 and 2 (black line)

High Resolution Mass Spectroscopy (HR-MS)

HR-MS: Calculated for $C_{29}H_{32}O_4$ [M+H]⁺: 445.2379, found: 445.2366 (100%).



Figure S2 HR-MS of compound A with $[M+H]^{+1}$ peak at 445.2366

NMR spectra of compound A



(a)



Figure S3 Solution phase (a) 1 H and (b) 13 C NMR spectra of compound A



Figure S4 UV-visible spectra of starting precursor organic molecules (a) biphenyl-4-carboxaldehyde and (b) 5, 5-dimethylcyclohexane-1, 3-dione (dimedone).

	Table S1	Crystallographic	parameters of compound B .
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Compound Name	Compound B
Chemical formula	$C_{29}H_{30}O_{3}$
Formula wt.	426.53
Crystal system	Monoclinic
Space group	$P2_{1}/c$
Т, К	296
<i>a</i> , Å	11.5533(5)
<i>b</i> , Å	10.2872(5)
<i>c</i> , Å	19.6885(9)
α, deg	90
β, deg	97.333(2)
γ, deg	90
Ζ	4
<i>V</i> , Å ³	2320.86(18)
$D_{calc}, \mathrm{gcm}^{-3}$	1.221
μ (mm ⁻¹)	0.078
reflns collected	19370
unique reflns	4154
$R_1 [I > 2(I)]$	0.0626
wR2 (all)	0.1788
GOF	1.101
Data collection	Bruker-Apex II
CCDC no.	1993303

The compound **B** on crystallizing from acetone resulted in block-shaped single crystal solved in monoclinic $P2_1/c$ space group with one molecule in the asymmetric unit. This cyclisation product has significantly different crystal packing arrangement. The biphenyl ring conformation is relatively planar compared to compound **A** with dihedral angle of 12.24°. Although the 3D crystal packing arrangement shows well separated biphenyl rings with herringbone type of molecular packing arrangements, the dimedone units of adjacent molecules are interacting with the biphenyl rings via weak C–H… π interactions as shown in Figure S5.



Figure S5 Herringbone type molecular packing of compound **B** with no possible $\pi \cdots \pi$ interactions between biphenyl groups. Although weak C–H $\cdots \pi$ interactions have been observed between biphenyl ring with dimedone units of adjacent molecules (crystal packing shown along bc plane).