

Supporting information for

# Mussel-inspired strategy for stabilizing ultrathin polymer films and its application to spin-on doping of semiconductors

*Reika Katsumata,<sup>†</sup> Ratchana Limary,<sup>‡</sup> Yuanyi Zhang,<sup>§</sup> Bhooshan C. Popere,<sup>†,§</sup> Andrew T. Heitsch,<sup>+</sup> Mingqi Li,<sup>||</sup> Peter Trefonas,<sup>||</sup> and Rachel A. Segalman<sup>\*†,§,O</sup>*

<sup>†</sup>Materials Research Laboratory, University of California, Santa Barbara, California 93106, United States

<sup>‡</sup>Lam Research Corporation, Austin, Texas 78753, United States

<sup>§</sup>Department of Chemical Engineering, University of California, Santa Barbara, California 93106, United States

<sup>+</sup>The Dow Chemical Company, Lake Jackson, Texas 77566, United States

<sup>||</sup>Dow Electronic Materials, Marlborough, Massachusetts 01752, United States

<sup>O</sup>Materials Department, University of California, Santa Barbara, California 93106, United States

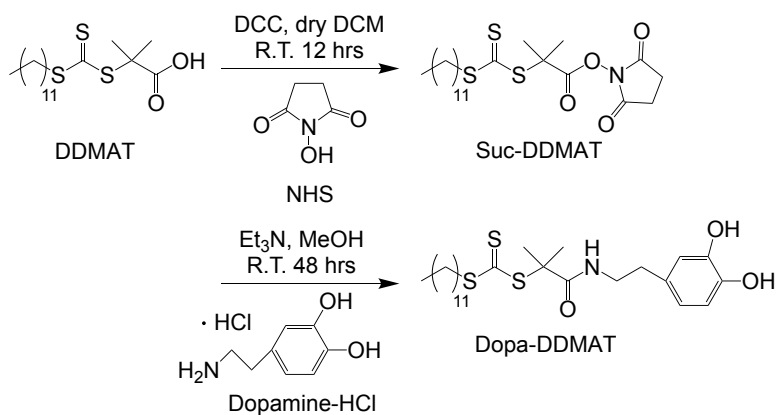
\*To whom correspondence should be addressed: segalman@engineering.ucsb.edu (R.A.S)

## TABLE OF CONTENTS

Synthesis of Dopa-functionalized RAFT transfer agent.....	2
NMR .....	3
Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) of RAFT transfer agent.....	5
Gel permeation chromatography (GPC) .....	6
Differential scanning calorimetry (DSC).....	7
Water contact angle tests of substrates .....	8
TGA .....	8
References.....	9

### Synthesis of Dopa-functionalized RAFT transfer agent

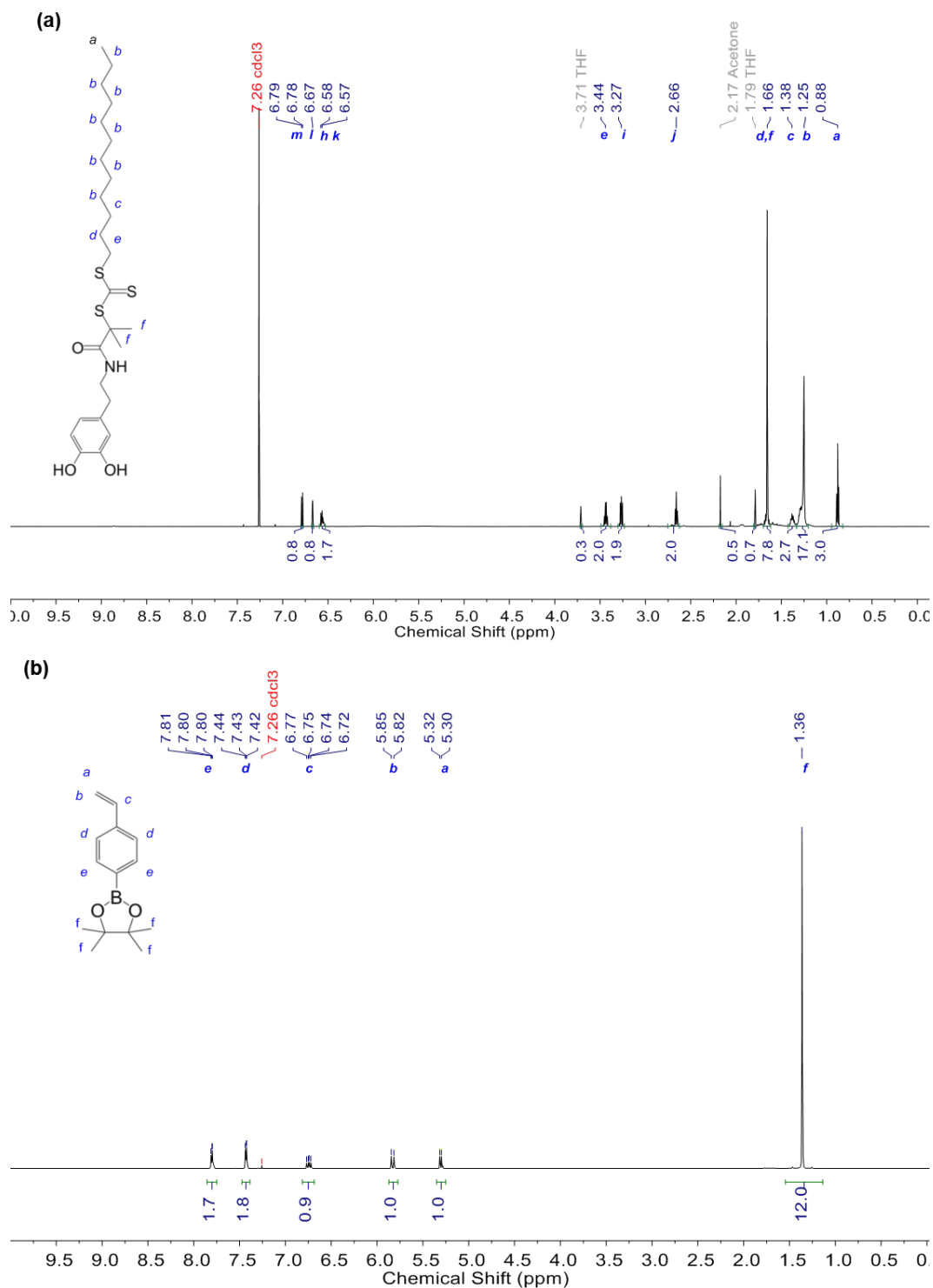
The reagents were purchased from either Sigma-Aldrich or ACROS Organics and used as received unless otherwise specified. Dopamine was covalently attached to a RAFT transfer agent (2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid: DDMAT) by a coupling reaction following a published procedure,<sup>1, 2</sup> and the reaction scheme is shown in **Figure S1**. First, *N*-hydroxysuccinimide (NHS)-modified DDMAT (Suc-DDMAT) was synthesized by a coupling reaction using *N,N*-dicyclohexylcarbodiimide (DCC). A suspension of NHS (1.036 g, 9 mmol) in dry dichloromethane (DCM, 40 mL) was prepared in a 100 mL round bottom flask. The suspension was added dropwise into a 250 mL Schlenk flask of a solution of DDMAT (2.188 g, 6 mmol), DCC (1.857 g, 9 mmol), and dry DCM (50 mL) while the flask was kept in an ice bath. The solution was allowed to come to room temperature and to react overnight, after which the DCM was removed under vacuum. The crude product was purified by silica gel chromatography (ethyl acetate: petroleum ether = 3:1) and the final product, Suc-DDMAT, was obtained as a yellow solid. As a second step, Suc-DDMAT (0.5118 g, 1.062 mmol) and dopamine hydrochloride (Dopamine-HCl, 0.2522 g, 1.329 mmol) were dissolved in 60 mL of methanol with triethylamine (200  $\mu$ L, 1.435 mmol) in a 100 mL round bottom flask, and reacted for 48 hrs at room temperature under a nitrogen atmosphere and in the dark. The product was dissolved in dimethyl ether, washed with water then brine, three times each, and the organic phase was dried over magnesium sulfate. After removing the residual solvent under vacuum, the Dopa-DDMAT was precipitated into cold hexanes and dried under vacuum (< 400 mTorr) overnight at room temperature to yield a yellow viscous liquid.



**Figure S1:** Synthesis scheme of Dopa-DDMAT.

## NMR

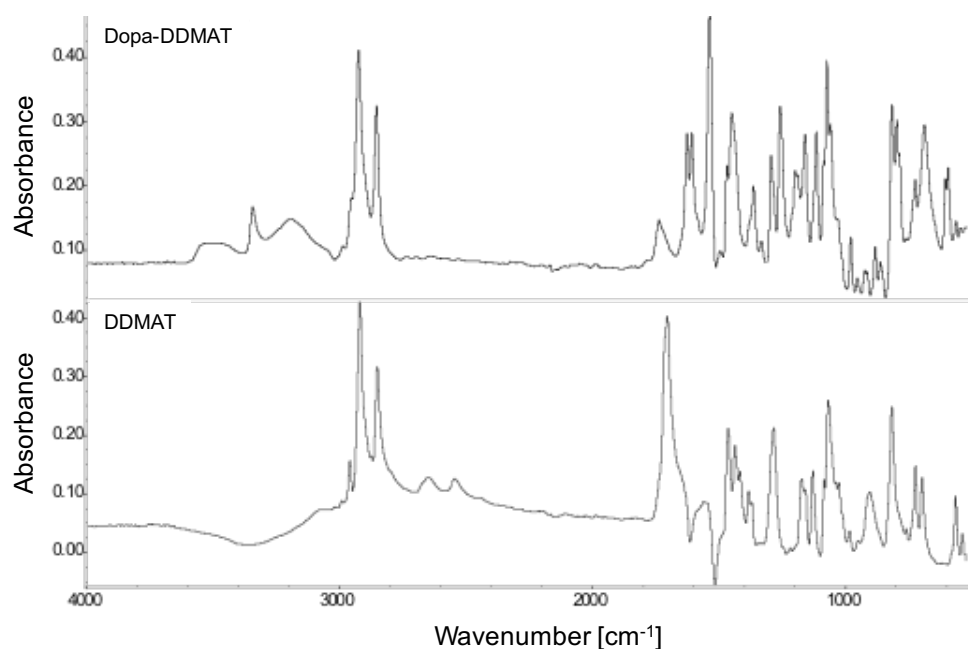
$^1\text{H}$  nuclear magnetic resonance (NMR) spectra were obtained using a 600 MHz SB Varian VNMRS NMR Spectrometer using deuterated chloroform as a solvent. Number averaged molecular weights ( $M_n$ ) were calculated by end group analysis based on **Figure S2c** and **d**, and the  $M_n$  is listed in **Table S1**.





### *Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) of RAFT transfer agent*

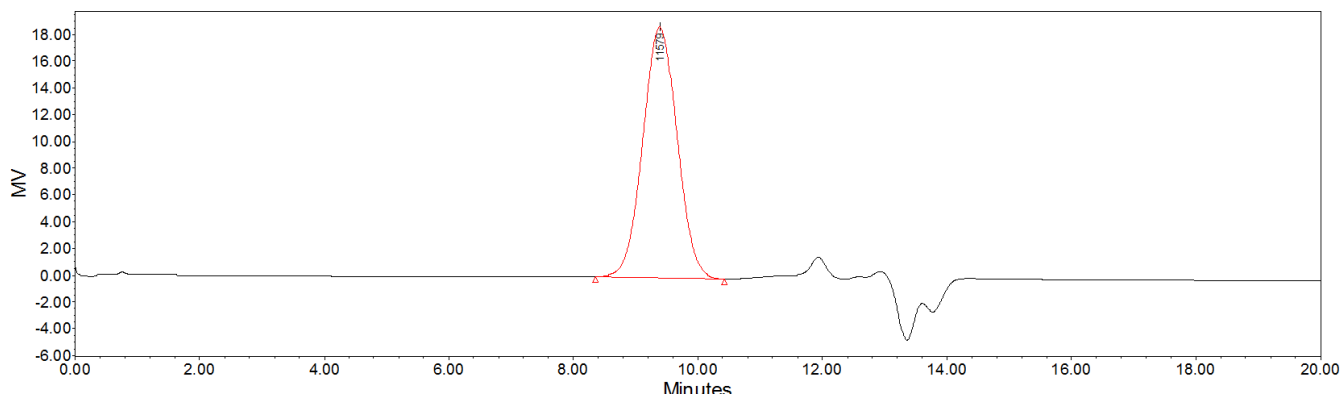
The successful synthesis of the Dopa-functionalized RAFT agent was confirmed by attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy using a Nicolet iS10 with a Smart Diamond ATR accessory. **Figure S3** shows ATR-FTIR spectra of Dopa-DDMAT and DDMAT. A broad peak around  $3200\text{ cm}^{-1}$  corresponds to the -OH vibration of phenol, which is unique to Dopa-DDMAT and consistent with a previous report.<sup>1</sup>



**Figure S3:** ATR-FTIR spectrum of dopamine-DDMAT. The broad peak at  $\sim 3200\text{ cm}^{-1}$  corresponds to the -OH vibration of the phenol, demonstrating the successful synthesis of dopamine-DDMAT.

### Gel permeation chromatography (GPC)

Number average molecular weight ( $M_n$ ) and dispersity ( $\mathcal{D}$ ) of PVBAPE-Control relative to polystyrene (PS) standards were determined by gel permeation chromatography (GPC, Waters instrument, 2414 refractive index detector) with Agilent PLgel 5  $\mu$ m MiniMIX-D columns. The eluent was tetrahydrofuran and the flow rate was 0.3 mL/min at 35 °C. The PVBAPE-Dopa was not able to be measured due to a strong interaction with the column. The estimated  $M_n$  and  $\mathcal{D}$  are listed in **Table S1**.



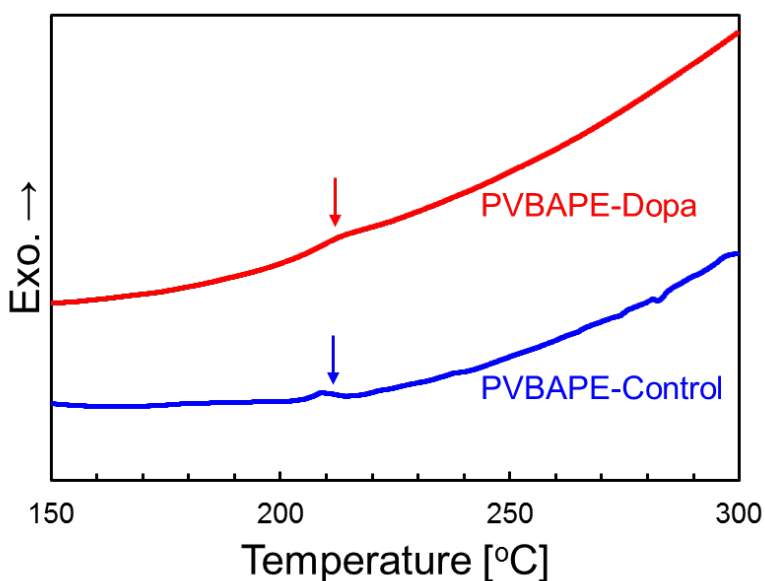
**Figure S4:** Refractive index signal of GPC for PVBAPE-Control.

**Table S1:**  $M_n$  and  $\mathcal{D}$  of PVBAPE-Control and PVBAPE-Dopa evaluated by NMR and GPC.

	PVBAPE-Control		PVBAPE-Dopa
	NMR	GPC	NMR
$M_n$ [kDa]	11.3	10.6	11.4
$\mathcal{D}$	n/a	1.16	n/a

### ***Differential scanning calorimetry (DSC)***

The glass transition temperature ( $T_g$ ) was evaluated via differential scanning calorimetry (DSC, PerkinElmer DSC 8000) in the second heating scan at 20 °C/min via the half delta  $C_p$  method. The  $T_g$ s of PVBAPE-Control and PVBAPE-Dopa were both evaluated as ~210 °C, indicating that  $T_g$  does not explain the different dewetting/wetting behavior of PVBAPE-Control and -Dopa in **Figure 2** in the main manuscript.



**Figure S5:** DSC curves of PVBAPE-Control and PVBAPE-Dopa.

### Water contact angle tests of substrates

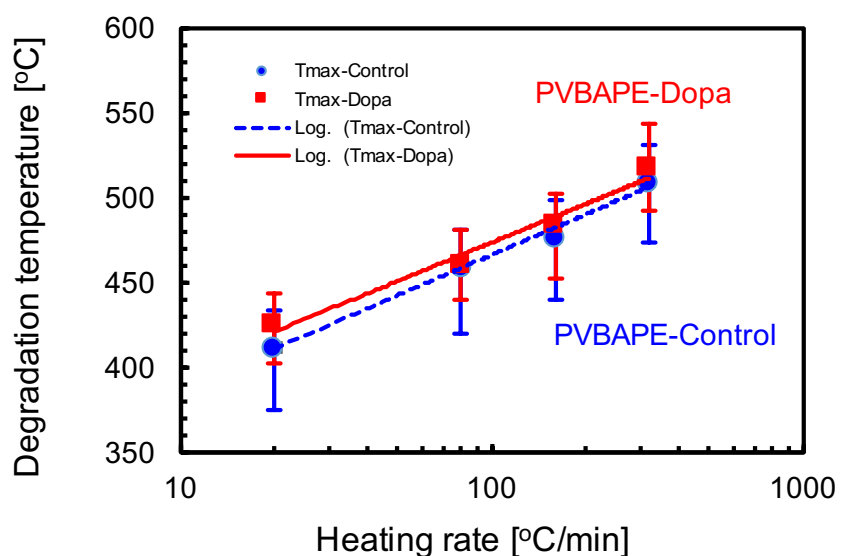
Static water contact angles were measured using a ramé-hart Model 290 advanced goniometer. The snapshots were taken within 10 sec after droplet deposition and evaluated by DROPImage Advanced. The volume of the deionized water was controlled to be 60  $\mu$ L. We would like to note that the water contact angle of Si-OH was too small to measure, and water contact values are listed in **Table S2**.

**Table S2:** Static water contact angle of substrates. The error corresponds to the standard deviation of 50 measurements, 10 at 5 different locations on the same sample.

Substrates	Si-OH	SiO <sub>x</sub>	Si <sub>3</sub> N <sub>4</sub>	TiN
Water contact angle [degree]	~0	49.6 $\pm$ 1.6	35.3 $\pm$ 4.9	82.1 $\pm$ 1.4

### TGA

Thermal gravity analysis (TGA) was conducted by Discovery TGA Thermo-Gravimetric Analyzer under nitrogen atmosphere. In an Aluminium oxide pan, 3–5 mg of PVBAPE-Control or PVBAPE-Dopa was heated from 50  $^{\circ}$ C to 950  $^{\circ}$ C with a wide range of heating rates (20–200  $^{\circ}$ C/min) to mimic RTA condition (6000  $^{\circ}$ C/min or 100  $^{\circ}$ C/sec). **Figure S6** shows onset (lower bottom of the error bars), end set (top of the error bars), and degradation temperature (Tmax) where the first derivative of weight with temperature reaches a maximum.



**Figure S6:** Degradation temperatures as a function of heating rate.



## **References**

1. Oyeneye, O. O.; Xu, W. Z.; Charpentier, P. A., Adhesive RAFT agents for controlled polymerization of acrylamide: effect of catechol-end R groups. *RSC Advances* **2015**, 5, (94), 76919-76926.
2. Zobrist, C.; Sobocinski, J.; Lyskawa, J.; Fournier, D.; Miri, V.; Traisnel, M.; Jimenez, M.; Woisel, P., Functionalization of Titanium Surfaces with Polymer Brushes Prepared from a Biomimetic RAFT Agent. *Macromolecules* **2011**, 44, (15), 5883-5892.