A *p*-Type PbS Quantum Dot Ink with Improved Stability for Solution Processable Optoelectronics

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Materials and synthesis methods: The following reagents for synthesis and subsequent ligand exchange were used as received. Lead(II) oxide (PbO, 99.9%), anhydrous toluene (99.8%), and 1,2-ethanedithhiol (EDT, 98%) were purchased from Alfa Aesar. Bis(trimethylsilyl) sulfide ((TMS)$_2$S, 95%) and 1-octadecene (ODE, 90%) were purchased from Acros Organics. For PR (Precipitation/re-dispersion) purification, methyl acetate (MeOAc, 99 %) purchased from Millipore Sigma was purged with nitrogen for 60 minutes and dried over activated 4A molecular sieves in a nitrogen glovebox.

PbS colloidal quantum dots were synthesized according to the previously reported method by Zhang et al.[1] with slight modifications. In particular, after synthesis, precipitated and re-dispersion (PR) were carried out under nitrogen atmosphere using anhydrous methyl acetate and *n*-octane respectively. The process was repeated twice to remove impurities and synthesis solvent. As-synthesized oleate capped PbS QDs have lowest energy electronic transition (LEET) peak centered at 880 nm (1.4 eV), indicating 2.8 nm diameter as estimated through a previously published sizing curve.[2]

Biphasic Ligand Exchange Process: In the bi-phasic ligand exchange process, 2 mL of 50 mg/mL of purified, oleate-capped PbS QDs in *n*-octane was added drop wise to 2 mL MeOH containing 0.205 g 3-MPA (~400x ligand/QD) while stirring at room temperature. The ligand exchange process completed within few seconds and quantum dots were transferred from octane into MeOH forming a dark brown polar phase. Octane supernatant was removed, 5 mL of fresh octane was added to wash PbS-MPA capped quantum dots, and the washing step was repeated three times to remove exchanged oleate/oleic acid ligands. After the final wash and separation of non-polar phase, 2 mL of toluene was added to the MeOH solution to promote flocculation of the 3-MPA capped QDs (we note that flocculation of the 3-MPA capped QDs in MeOH solution occurs slowly even in the absence of toluene). The mixture was centrifuged at 4000 rpm for 10 min to pull down the QDs, and the supernatant was decanted away. The QDs were then dried under flowing nitrogen, and 2 mL of BnzAm was added (or, in a control experiment, 2 mL butylamine). After stirring the PbS-MPA and BnzAm mixture, QDs were centrifuged at 10000 rpm for five minutes to get rid of any undissolved particulates and filtered through 0.1 µm PTFE filter before spin coating on devices. Typically, the QD/BnzAm ink was obtained with a final concentration of ~40 mg/mL.

NMR spectroscopy: ^{1}H NMR of the PbS-MPA in benzylamine and all DOSY measurements were performed on a Bruker Avance III-HD 500 MHz spectrometer. Reference spectra to aid in peak assignment were recorded on a Bruker Avance III-HD 400 MHz spectrometer. Measurements of the ink were conducted directly on the sample at ~40 mg/mL PbS QDs in normal-abundance (proteo) benzylamine, and employed 16 acquisitions with 30s delay. Measurements for MPA/benzylamine mixtures were conducted similarly and chemical shift was referenced to a tetramethylsilane (TMS) external standard. Reference spectra for MPA and benzylamine in methanol were recorded in methanol-d$_4$ and referenced to the methanol residual CH$_3$ peak and a TMS internal standard respectively.

Device Fabrication: ITO coated glass substrates with area ~2 cm^2 were cleaned by washing with detergent and then sequentially sonicated in acetone, IPA, ethanol, and dionized water for 5 minutes each before drying by nitrogen flow. Three drops of 5% tetrabutyl titanate solution in dry ethanol were spin coated at 4000 rpm. These coated substrates were annealed at 450°C for 30 minutes to form compact TiO$_2$ films and were used for photovoltaic device fabrication without further treatment. 15 µL of PbS-MPA solution was dropped and spread on entire substrate by spinning at 1500 rpm for 30 s, followed by annealing at 90° and left in glove box to dry. The process was repeated to make a ~200 nm thick film. Each layer was annealed at 90°C for five minutes before subsequent coating. The top Au-contacts were deposited using MDC e-Vap 4000 Electron Beam Evaporation System with a base pressure 1×10^{-6} torr through a shadow mask. The shadow mask also defines the active area of the devices. Au metal was deposited at a rate of 2Å/s to get a final metal thickness of 100nm. Similarly, conductive PbS QD films were fabricated onto a prepatterned SiO$_2$-coated silicon substrates by spinning 15 uL QD solution yielding a 170nm think film for lateral devices to measure sheet resistance and photoconductivity. While spin coating and annealing were conducted under nitrogen, all electronic measurements were done at room temperature and under ambient atmosphere.
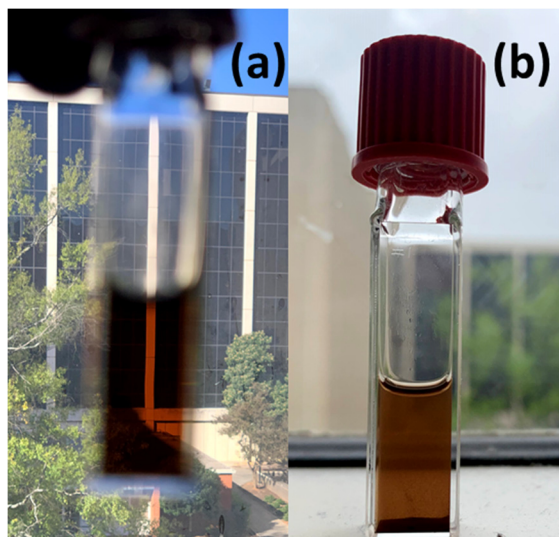
Figure S1. (a) Well-dispersed solution of PbS-MPA QDs in Benzylamine (b) PbS-MPA in butylamine failed to produce a stable and well-dispersed colloidal solution.
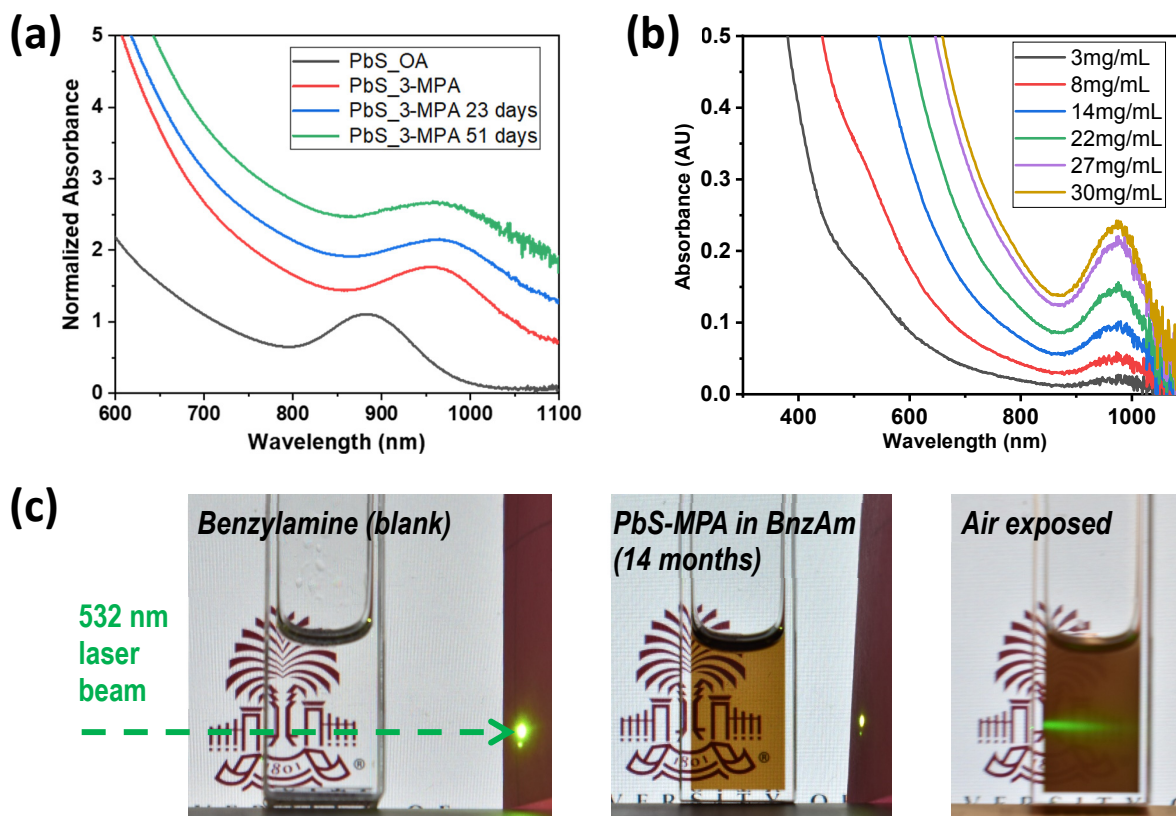
Figure S2. (a) UV-Vis Absorbance of QDs as-synthesized (diluted in *n*-octane) and post ligand exchange (diluted in BnzAm) over the period of 51 days (normalized at lowest-energy peak minus background; PbS-MPA spectra are vertically offset for clarity). (b) UV-Vis Absorbance of MPA capped QDs for series of dilutions in benzylamine solvent. (c) PbS-MPA in BnzAm remains well dispersed with negligible light scattering after 14 months. Center photo shows ink diluted in additional dry BnzAm after storage at room temperature under ambient light, in inert atmosphere. We note that the sample is not stable to air exposure; air exposure leads to a hazy appearance within a few hours.
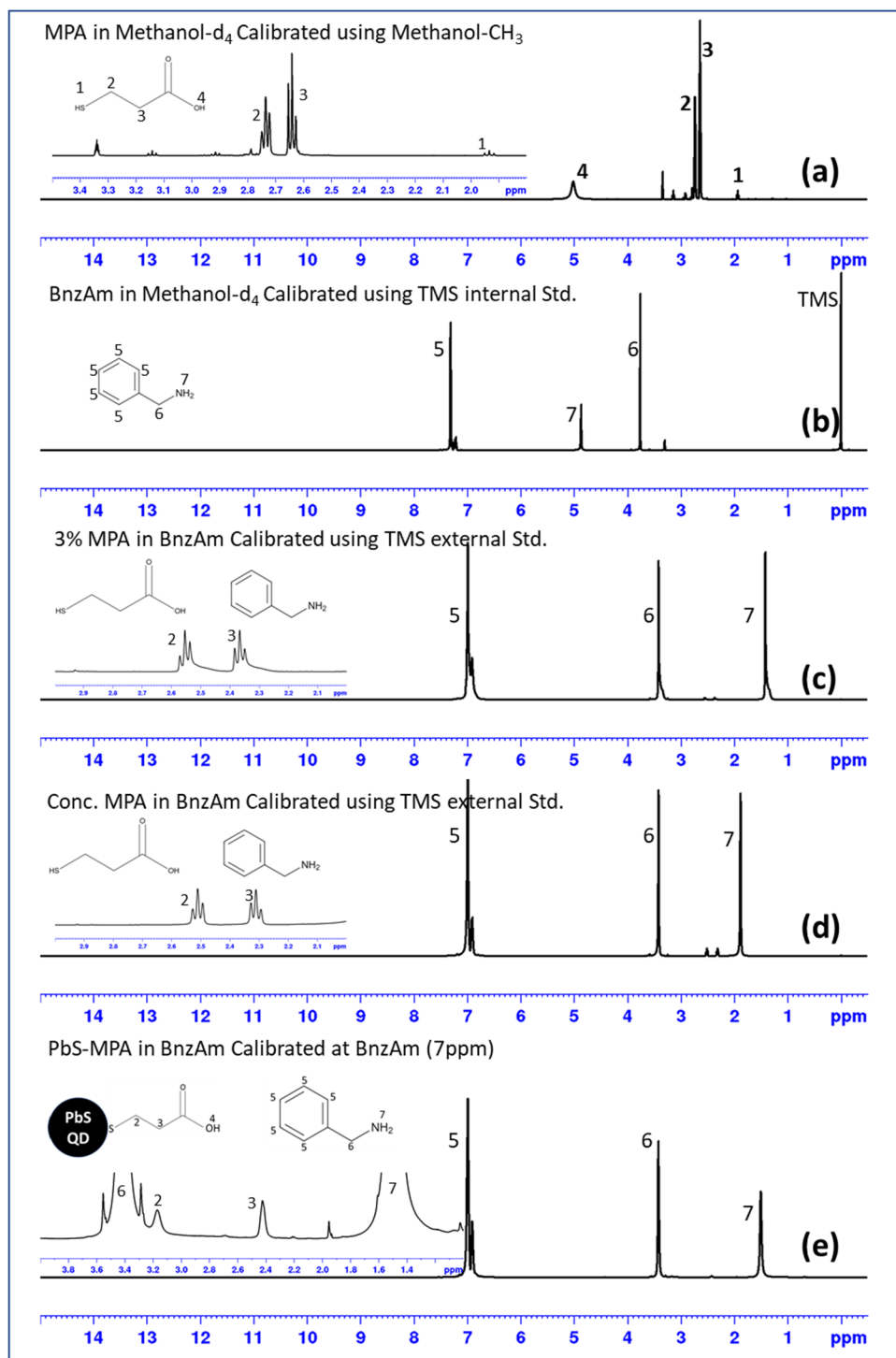
Figure S3. Full scale ^{1}H NMR spectra. (a) Peak assignments for MPA in methanol-d_4 were made as follows: multiplets at δ = 2.65 ppm and δ = 2.74 ppm correspond to the methylene protons nearest to and farthest from the thiol group, respectively. These assignments are also consistent with findings by Reinhart et al. for MPA in DMSO-d_6.[3] (b) Peak assignments for benzylamine in methanol-d_4, in which NH$_2$ exchanges with the solvent. (c,d) Spectra for 3% MPA and a higher concentration (~10%) respectively in proteo-benzylamine. We note that in the MPA methylene peak positions are nearly identical to those in methanol-d_4, and we make the same assignment. (e) ^{1}H NMR spectrum of the ink (as shown in Fig. 3). The free MPA peaks are absent, and broadened resonances are found at δ = 2.42 ppm and δ = 3.17 ppm. We assign the peak at δ = 3.17 ppm to the methylene protons nearest the thiol on the basis of its greater shift and broadening (as expected for ligands bound to QD surfaces).
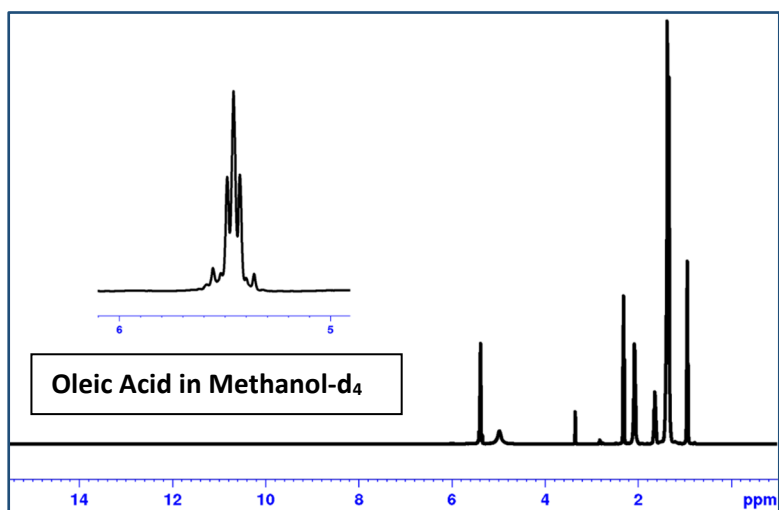
Figure S4. Full scale ^{1}H NMR spectra of oleic acid in methanol-d$_4$: inset shows the olefinic proton peaks.
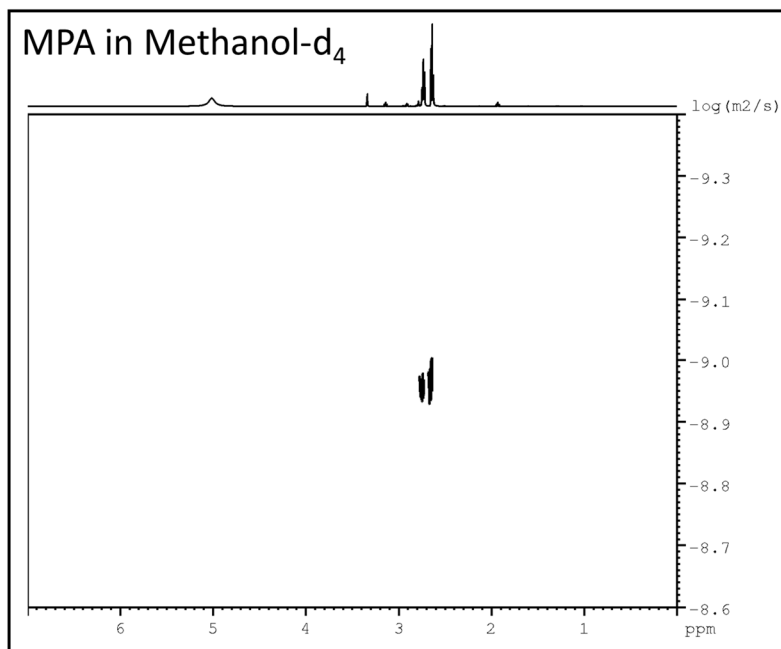

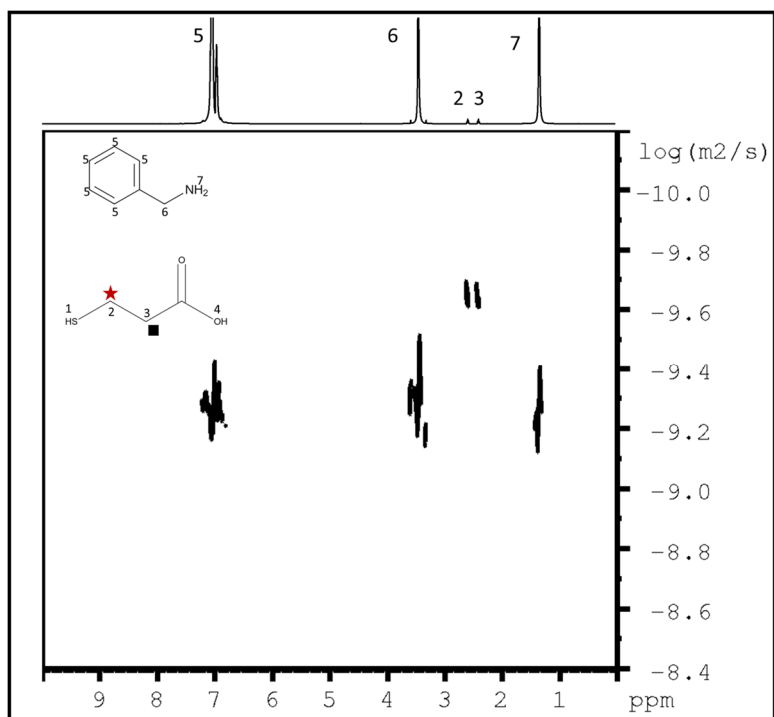**Figure S5.** DOSY of free MPA in methanol-d$_4$.

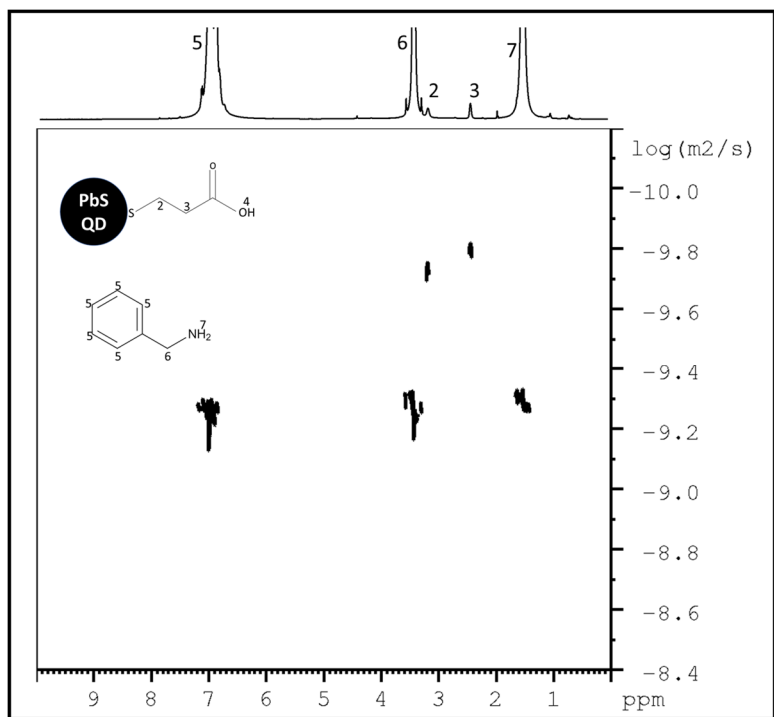**Figure S6.** DOSY of free MPA in Benzylamine.

Figure S7. DOSY of PbS-MPA QDs in Benzylamine.

Effective diffusion constant and hydrodynamic size of MPA in PbS-MPA ink. The hydrodynamic radius of methanol was estimated to be 0.215 nm using the Stokes equation based on a standard DOSY experiment in D_2O. Effective hydrodynamic radii of other species were calculated based on the following equation:

$$\frac{D_S}{D_{ref}} = \frac{R_{ref}}{R_S}$$

Where: D_S, D_{ref} are measured diffusion coefficients and R_{ref} and R_s are hydrodynamic radius of sample and reference respectively. This approach was used to obtain R_s=0.34 nm for MPA in methanol from Fig. S5, and was likewise used to assign the effective R_s for MPA in the PbS-MPA ink by comparison of D for the MPA methylene resonances for free MPA and PbS-MPA in benzylamine solvent as listed in Table S1.

Table S1. Diffusion constants of different samples measured by DOSY

System	D_{BnzAm} 10^{-10} m^2/s	D_{MPA} 10^{-10} m^2/s	$R_{s,MPA}$ nm
MPA in BnzAm solvent	5.5	2.25	0.34
PbS-MPA in BnzAm solvent	5.4	1.25	0.61

References

1 J. Zhang, R. W. Crisp, J. Gao, D. M. Kroupa, M. C. Beard and J. M. Luther, *J. Phys. Chem. Lett.*, 2015, **6**, 1830–1833.
2 I. Moreels, K. Lambert, D. Smeets, D. De Muynck, T. Nollet, J. C. Martins, F. Vanhaecke, A. Vantomme, C. Delerue and G. Allan, *ACS Nano*, 2009, **3**, 3023–3030.
3 C. C. Reinhart and E. Johansson, *Chem. Mater.*, 2015, **27**, 7313–7320.