

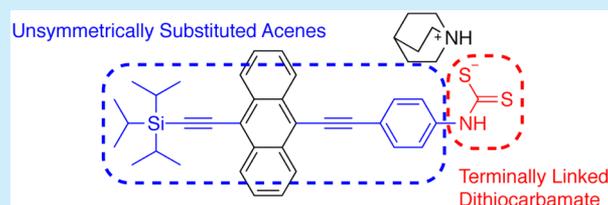
Synthesis and Properties of Dithiocarbamate-Linked Acenes

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Supporting Information

ABSTRACT: A small set of unsymmetrically substituted acene derivatives containing either aniline or dithiocarbamate moieties was synthesized. A stepwise, one-pot procedure was used to transform appropriate acenequinones to aniline-linked acenes in one step with moderate yields. A heretofore-unreported carbon disulfide activation process involving the formation of a trialkylammonium dithiocarbamate intermediate was found to be essential to convert these acene anilines to acene dithiocarbamates. The effects of the aniline and dithiocarbamate moieties on the photophysical properties of selected acene chromophores were assessed by UV/vis absorption and fluorescence spectroscopies.



Acenes, such as anthracene, tetracene, and pentacene, display competitive rates of intersystem crossing between singlet and triplet excited states,¹ both in dilute solutions and in various condensed phases,² even in the absence of carbonyl or heavy atom moieties. This ability to interconvert between high-spin and low-spin excitonic states enables acenes to participate in a plethora of intellectually interesting and practical arenas, such as singlet fission,³ photon upconversion,⁴ and singlet oxygen generation.⁵

Composites and heterojunctions of acenes with metal chalcogenide nanocrystals, in particular, display rich photophysical complexity and utility.⁶ For example, a solar cell based on a pentacene/PbSe quantum dot (QD) planar heterojunction demonstrated enhanced external quantum efficiencies owing to singlet fission in the pentacene layer followed by triplet transfer at the acene–QD interface.⁷ A thin-film composite of tetracene and PbS QDs displayed direct triplet energy transfer from tetracene to PbS QDs via a posited Dexter energy transfer mechanism.⁸ In a mirrored scenario, anthracene-capped colloidal CdSe QDs demonstrated direct triplet transfer from the CdSe QDs to the acene,⁹ which can be followed by triplet–triplet annihilation to effect photon upconversion¹⁰ and/or singlet oxygen generation.

As is generally characteristic of organic–inorganic hybrid systems, the nature of the acene–nanocrystal interface strongly influences the photophysical properties of the composite.^{6a,11} For instance, the aforementioned triplet transfer from colloidal CdSe QDs to anthracene was accomplished when anthracene-9-carboxylic acid was anchored to a CdSe QD through the carboxylic acid binding moiety, but triplet transfer was not observed between CdSe QDs and anthracene itself.⁹

To date, most experimental approaches to tuning the acene–QD interface involve changing the passivating organic ligand shell surrounding each nanocrystal.¹² The other conceptual approach to interface tuning, installing and changing binding groups on the acene, is synthetically taxing and, therefore, underexplored.

Herein, we report the facile preparation of what we believe to be a new class of aniline- and dithiocarbamate-linked acene ligands for semiconductor nanocrystals. These acene ligands will enable

the controlled synthesis of a library of semiconductor nanocrystal–chromophore model systems to study a host of fundamental energy transfer, exciton dissociation, and multi-exciton interactions in hybrid materials.

Figure 1 shows the structural features that we targeted in this work. Three acene cores were pursued on the basis of their recurrence in the aforementioned acene–nanocrystal composites: anthracenes, tetracenes, and pentacenes. Unsymmetrically

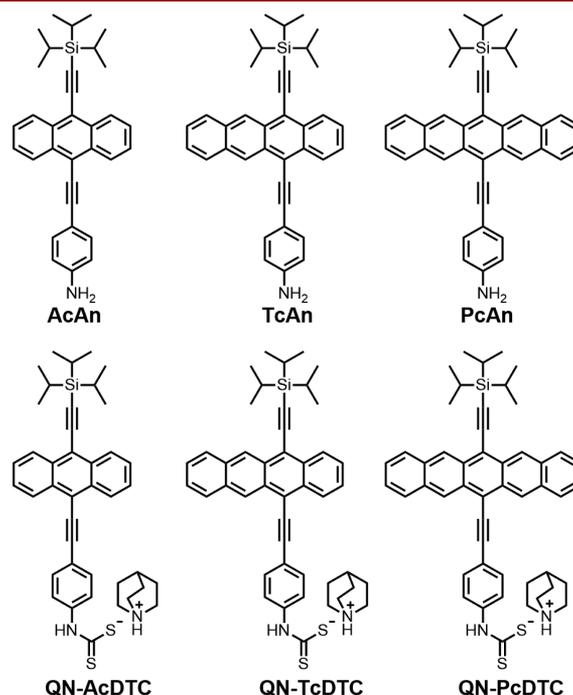


Figure 1. Structures of the acene ligands reported in this paper.

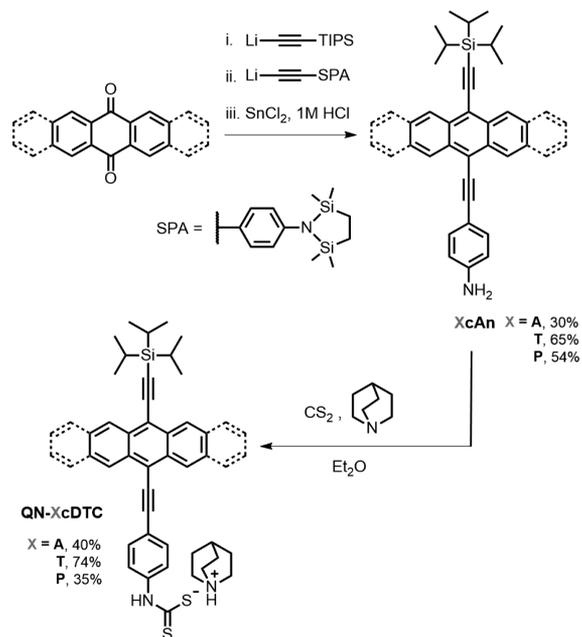
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substituted acene cores were pursued so that each acene ligand contained only one anchoring group. Aryl- or alkylethynyl substitution on the ring that displays the largest frontier orbital coefficients (for instance, at the 9,10-position of anthracene) is the most successful strategy to increase the stability, solubility, and processability of acenes.¹³ Anilines¹⁴ and dithiocarbamates (DTCs)¹⁵ are known to act as moderate and strong ligands, respectively, for CdSe QDs. More interestingly, the dithiocarbamate anchoring group was uniquely observed to facilitate electronic wave function mixing and/or charge transfer between the QD and the organic ligand,¹⁵ unlike other anchoring groups, such as carboxylic acids, phosphonic acids, and anilines, that only allow for through-space dipolar resonant energy transfer between the CdSe QD and a ligand.^{9,16} Therefore, both aniline- and DTC-linked acenes were pursued in this work; conveniently, the aniline-linked acenes served as synthetic precursors for the dithiocarbamate-linked acene ligands. Lastly, we posited that installing the aniline or dithiocarbamate binding moiety at the *para*-position of the phenyl ring will allow easy access for nanocrystal binding while still maintaining conjugation with the acene backbone.

Scheme 1 shows the general synthetic route to access the unsymmetrically substituted acene ligands reported in this work,

Scheme 1. Synthesis of the Unsymmetric Aniline- and Dithiocarbamate-Linked Diethynylacenes

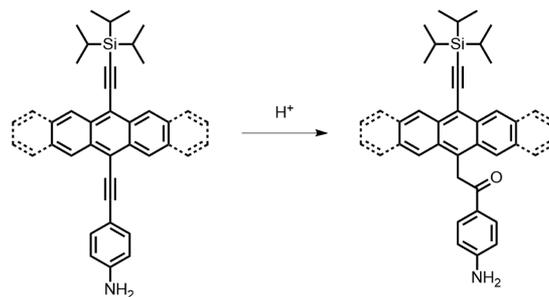


which was adapted from Tykwinski's one-pot procedure to access unsymmetrically substituted acenes.¹⁷ For the aniline-linked acenes (**AcAn**, **TcAn**, **PcAn**), we started with cannula addition of 1 equiv of a (trisopropylsilyl)ethynyllithium solution to a suspension of the appropriate acenequinone at $-78\text{ }^{\circ}\text{C}$, followed by addition of lithiated stabase-protected ethynylaniline (SPEA) without the isolation of the γ -hydroxy ketone intermediate formed in the previous step. Following this addition, reduction was effected by adding SnCl₂ in aqueous acid at room temperature, which also effects quantitative hydrolysis of the stabase protecting group to reveal the aniline-linked acenes upon workup. Even though four separate transformations were carried out in one pot, pure **AcAn**, **TcAn**, and **PcAn** were isolated in 30%,

65%, and 54% yield, respectively, from the corresponding acenequinones after flash column chromatography.

The reductive aromatization step en route to forming **AcAn**, **TcAn**, and **PcAn** suffered from low product yields, even though this transformation typically proceeds with high yields.¹⁸ An aryl acene ketone byproduct (Scheme 2) was consistently observed.

Scheme 2. Undesired Hydrolyzation of Aniline-Linked Acenes under Acidic Conditions



The formation of these compounds was ascribed to alkyne hydration in acidic aqueous solutions, which can be promoted in the presence of a soft, Lewis acidic metal center (Sn). The electron-donating amino substituent likely promotes this undesired side reaction as well.

The aniline moieties of **AcAn**, **TcAn**, and **PcAn** were converted into dithiocarbamate (DTC) moieties by reaction with carbon disulfide and a trialkylamine base at room temperature. Using DABCO or quinuclidine as the amine base resulted in the highest percent conversions. We suspect that DABCO and quinuclidine activate CS₂ for subsequent nucleophilic attack by aniline by forming a trialkylammonium dithiocarbamate intermediate.¹⁹ Although large excesses of DABCO and CS₂ were used, approximately 10% of the starting aniline acenes was consistently observed to remain unreacted in the crude reaction mixture by ¹H NMR analysis. The persistence of unreacted starting material was attributed to protonation of the ethynylaniline moiety, perhaps by the conjugate acid of DABCO, [DABCO-H]⁺, which is formed during the reaction. Consistent with this hypothesis, higher isolated yields of pure quinuclidinium dithiocarbamate acenes were obtained compared to the [DABCO-H]⁺ counterparts, since the conjugate acid of quinuclidine has a higher pK_a value (9.8) in DMSO compared to DABCO. The DTC acenes were isolated and purified by addition of excess triethylamine to the reaction mixture, followed by serial precipitation with CH₂Cl₂/hexanes and centrifugation. The quinuclidinium DTC acenes exhibited quantitative retention of the quinuclidinium counterion upon purification with triethylamine, and the unreacted precursor acenes were simply removed through centrifugation and washing with diethyl ether. In this fashion, **QN-AcDTC**, **QN-TcDTC**, and **QN-PcDTC** were isolated in 40%, 74%, and 35% yield, respectively, from the corresponding aniline precursors.

We characterized each acene by electronic absorbance (Figure 2) and fluorescence spectroscopy in CH₂Cl₂ at room temperature (Figure 3); Table 1 summarizes the results of these experiments. Each spectrum has a sharp, intense absorbance band in the ultraviolet region and a lower energy band that shows a series of vibronic peaks characteristic of linear acenes.^{13,18} UV-vis spectra of the DTC acene derivatives (**QN-AcDTC**, **QN-TcDTC**, and **QN-PcDTC**) are mostly analogous to the aniline derivatives (**AcAn**, **TcAn**, and **PcAn**). The aniline-linked acenes displayed slightly red-shifted absorbance maxima relative to the corre-

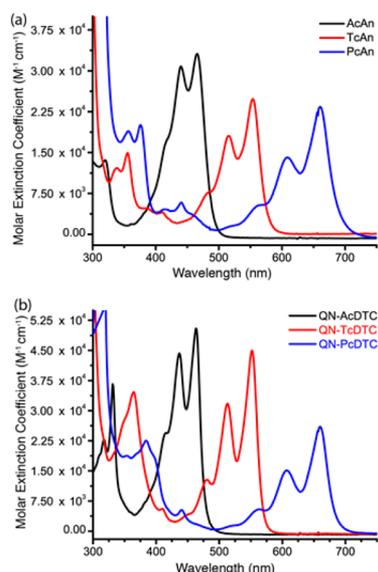


Figure 2. UV-vis absorbance spectra of (a) aniline-linked acenes and (b) dithiocarbamate-linked acenes in dichloromethane.

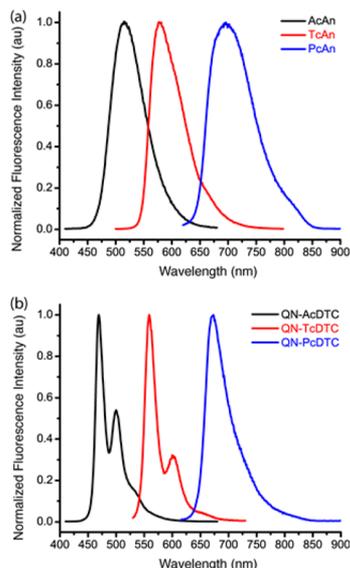


Figure 3. Normalized fluorescence spectra of (a) aniline-linked acenes and (b) dithiocarbamate-linked acenes in dichloromethane.

sponding DTC derivatives, which is ascribed to the strong electron-donating effect of the amino substituent. The DTC-linked acenes have better-resolved vibronic patterns in the absorbance traces; we attribute the broadening of the aniline derivatives to the low rotation barriers of arylethynyl groups enabling a large variety of accessible conformations with different excitation energies.

Table 1. Photophysical Parameters of Acenes in CH_2Cl_2

compd	$\lambda_{\text{onset,abs}}$ nm (eV)	$\lambda_{\text{max,abs}}$ (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	$\lambda_{\text{max,fl}}$ (nm)	Φ_f	τ (ns)
AcAn	490 (2.53)	276, 320, 466	33100	515	0.62	3.45
TcAn	581 (2.13)	293, 355, 554	24800	577	0.3	6
PcAn	692 (1.79)	313, 376, 661	23300	696	0.004	4.76
QN-AcDTC	478 (2.59)	274, 331, 463	50400	469	0.73	2.57
QN-TcDTC	568 (2.18)	292, 364, 552	44900	559	0.49	7.34
QN-PcDTC	683 (1.81)	316, 384, 660	26000	673	0.07	3.23

The optical HOMO–LUMO gaps of the DTC acenes are nearly identical to the aniline counterparts, indicating minimal aromatic stabilization resulting from dithiocarbamate substitution. The extinction coefficients of the DTC acene derivatives are slightly higher than those of the aniline acenes.

The fluorescence spectra of the DTC acene derivatives are significantly different compared to those of the aniline acenes. The DTC acenes have better-resolved and hypsochromically shifted fluorescence bands compared to their aniline counterparts (Figure 3). Clear (0,1) bands are observed in the emission spectra of smaller acenes (QN-AcDTC and QN-TcDTC), while the larger QN-PcDTC only has a broad (0,0) band that is sharper compared to PcAn. The trend in the blue shift of fluorescence maxima increases in the order of $\text{Pc} < \text{Tc} < \text{Ac}$, implying that the DTC substituent has a greater effect on the electronic structure of smaller acenes. The fluorescence quantum yields of both DTC and aniline acenes decreases with lengthening acene cores. It is noteworthy that the fluorescence quantum yield of QN-AcDTC ($\Phi_f = 0.73$) is higher than most reported diethynyl-substituted anthracenes, and QN-AcDTC also has the smallest Stokes' shift (6 nm) among all acenes studied in this work. These observations are ascribed to the stronger influence of the DTC substituent on the rigidity and electronic structure of smaller acenes.

Pilot experiments to test the efficacy of the acenes reported herein as ligands for metal chalcogenide nanocrystals were carried out using colloidal phosphine oxide-capped CdSe QDs and QN-PcDTC, following a previously reported procedure to obtain dithiocarbamate-capped colloidal nanocrystals.¹⁵ Figure 4 shows

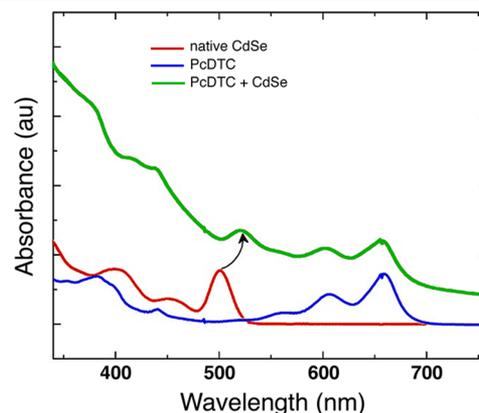


Figure 4. Absorbance spectra of PcDTC-capped CdSe QDs after 24 h of ligand exchange with QN-PcDTC in CH_2Cl_2 followed by serial precipitation and washing.

the absorbance spectrum of the pentacene DTC-capped CdSe QDs obtained after ligand exchange and three precipitation-washing cycles to remove excess or unbound ligand. Features arising from both the pentacene S_0 – S_1 transition and CdSe excitonic band can be observed, indicating that ligand exchange

occurred. Notably, the CdSe excitonic peak red-shifted from 501 nm in the native QD sample to 521 nm in the pentacene DTC-capped sample, which suggests that the CdSe exciton is slightly relaxed due to conjugation to the DTC anchoring group.¹⁵ This relaxation of exciton confinement should lead to favorably stronger optical coupling between the QD and acene components.⁶

In conclusion, we prepared new dithiocarbamate-linked acene derivatives and studied the influence of the DTC substituents on their photophysical properties. An activation process for CS₂ involving formation of a trialkylammonium dithiocarbamate intermediate plays a crucial role in the conversion of the aniline to the dithiocarbamate. This work significantly broadens the structural space of acene derivatives that may find practical use in forming organic molecule–QD hybrid materials. Functionalization of colloidal CdSe and PbS quantum dots and quantum dot films with this set of acene ligands and thorough photophysical characterization of the resulting hybrid materials are underway, and these results will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.orglett.6b03492](https://doi.org/10.1021/acs.orglett.6b03492).

Experimental procedures, characterization data, and NMR spectra of new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, CA, 1991; pp 186–187.
- (2) Walker, B. J.; Musser, A. J.; Beljonne, D.; Friend, R. H. *Nat. Chem.* **2013**, *5*, 1019–1024.
- (3) (a) Paci, I.; Johnson, J. C.; Chen, X.; Rana, G.; Popović, D.; David, D. E.; Nozik, A. J.; Ratner, M. A.; Michl, J. *J. Am. Chem. Soc.* **2006**, *128*, 16546–16553. (b) Aryanpour, K.; Shukla, A.; Mazumdar, S. *J. Phys. Chem. C* **2015**, *119*, 6966–6979. (c) Roberts, S. T.; McAnally, R. E.; Mastron, J. N.; Webber, D. H.; Whited, M. T.; Brutchey, R. L.; Thompson, M. E.; Bradforth, S. E. *J. Am. Chem. Soc.* **2012**, *134*, 6388–6400.
- (4) (a) Parker, C. A.; Hatchard, C. G. *Proc. R. Soc. London, Ser. A* **1962**, *269*, 574–584. (b) Singh-Rachford, T. N.; Castellano, F. N. *Coord. Chem. Rev.* **2010**, *254*, 2560–2573.
- (5) Zhang, J.; Sarrafpour, S.; Haas, T. E.; Müller, P.; Thomas, S. W., III. *J. Mater. Chem.* **2012**, *22*, 6182–6189.
- (6) (a) Agranovich, V.; Gartstein, Y.; Litinskaya, M. *Chem. Rev.* **2011**, *111*, 5179–5214. (b) Zhang, Q.; Atay, T.; Tischler, J. R.; Bradley, M. S.; Bulovic, V.; Nurmikko, A. V. *Nat. Nanotechnol.* **2007**, *2*, 555–559.
- (7) (a) Ehrler, B.; Walker, B. J.; Böhm, M. L.; Wilson, M. W. B.; Vaynzof, Y.; Friend, R. H.; Greenham, N. C. *Nat. Commun.* **2012**, *3*, 1019. (b) Tabachnyk, M.; Ehrler, B.; Gelin, S.; Böhm, M. L.; Walker, B. J.;

Musselman, K. P.; Greenham, N. C.; Friend, R. H.; Rao, A. *Nat. Mater.* **2014**, *13*, 1033–1038.

(8) Thompson, N. J.; Wilson, M. W. B.; Congreve, D. N.; Brown, P. R.; Scherer, J. M.; Bischof, T. S.; Wu, M.; Geva, N.; Welborn, M.; Van Voorhis, T.; et al. *Nat. Mater.* **2014**, *13*, 1039–1043.

(9) Mongin, C.; Garakyaraghi, S.; Razgoniaeva, N.; Zamkov, M.; Castellano, F. N. *Science* **2016**, *351*, 369–372.

(10) Wu, M.; Congreve, D. N.; Wilson, M. W. B.; Jean, J.; Geva, N.; Welborn, M.; Van Voorhis, T.; Bulović, V.; Bawendi, M. G.; Baldo, M. A. *Nat. Photonics* **2015**, *10*, 31–34.

(11) Jadhav, P. J.; Brown, P. R.; Thompson, N.; Wunsch, B.; Mohanty, A.; Yost, S. R.; Hontz, E.; Van Voorhis, T.; Bawendi, M. G.; Bulović, V.; Baldo, M. A. *Adv. Mater.* **2012**, *24*, 6169–6174.

(12) Chuang, C.-H. M.; Brown, P. R.; Bulović, V.; Bawendi, M. G. *Nat. Mater.* **2014**, *13*, 796–801.

(13) (a) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482–9483. (b) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15–18. (c) Watanabe, M.; Chang, Y. J.; Liu, S.-W.; Chao, T.-H.; Goto, K.; Islam, M.; Yuan, C.-H.; Tao, Y.-T.; Shinmyozu, T.; Chow, T. J. *Nat. Chem.* **2012**, *4*, 574–578.

(14) Donakowski, M. D.; Godbe, J. M.; Sknepnek, R.; Knowles, K. E.; de la Cruz, M. O.; Weiss, E. A. *J. Phys. Chem. C* **2010**, *114*, 22526–22534.

(15) (a) Frederick, M. T.; Weiss, E. A. *ACS Nano* **2010**, *4*, 3195–3200. (b) Frederick, M. T.; Amin, V. A.; Swenson, N. K.; Ho, A. Y.; Weiss, E. A. *Nano Lett.* **2013**, *13*, 287–292.

(16) Walker, B. J.; Nair, G. P.; Marshall, L. F.; Bulović, V.; Bawendi, M. G. *J. Am. Chem. Soc.* **2009**, *131*, 9624–9625.

(17) (a) Lehnher, D.; Gao, J.; Hegmann, F. A.; Tykewski, R. R. *Org. Lett.* **2008**, *10*, 4779–4782. (b) Lehnher, D.; McDonald, R.; Tykewski, R. R. *Org. Lett.* **2008**, *10*, 4163–4166.

(18) Zhang, J.; Smith, Z. C.; Thomas, S. W. *J. Org. Chem.* **2014**, *79*, 10081–10093.

(19) Baidya, M.; Kobayashi, S.; Brotzel, F.; Schmidhammer, U.; Riedle, E.; Mayr, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 6176–6179.