SUPPLEMENTARY INFORMATION

Supramolecular host-guest complexation of Lash's calix[4]azulene with tetraalkylammonium salts: binding and DFT computational studies

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Table of Contents

Table S1. Summary of association constants determined using Thordarson's *fittingprogram*[2a,b] from the Uv-vis titrations of the respective tetraalkylammonium halides and fluoroborate.

Entry	Salts	fittingprogram					Comments	
		Association constant (K / M-1)					Quality of fit (covfit)	
		Run 1	Run 2	Average	ASFU	STDV	Run 1	Run 2
1	TMACl	7371	7435	7400	0.44%	46	0.030	0.024
2	TMABr	3873	3772	3820	1.3%	72	0.020	0.020
3	TMAI	2802	2870	2840	1.2%	48	0.015	0.016
4	$TMABF_4$	5851	5994	5920	1.2%	100	0.028	0.024
5	$TEABF_4$	4988	5139	5060	1.5%	107	0.032	0.015
6	$TBABF_4$	3577	3669	3620	1.3%	65	0.010	0.013

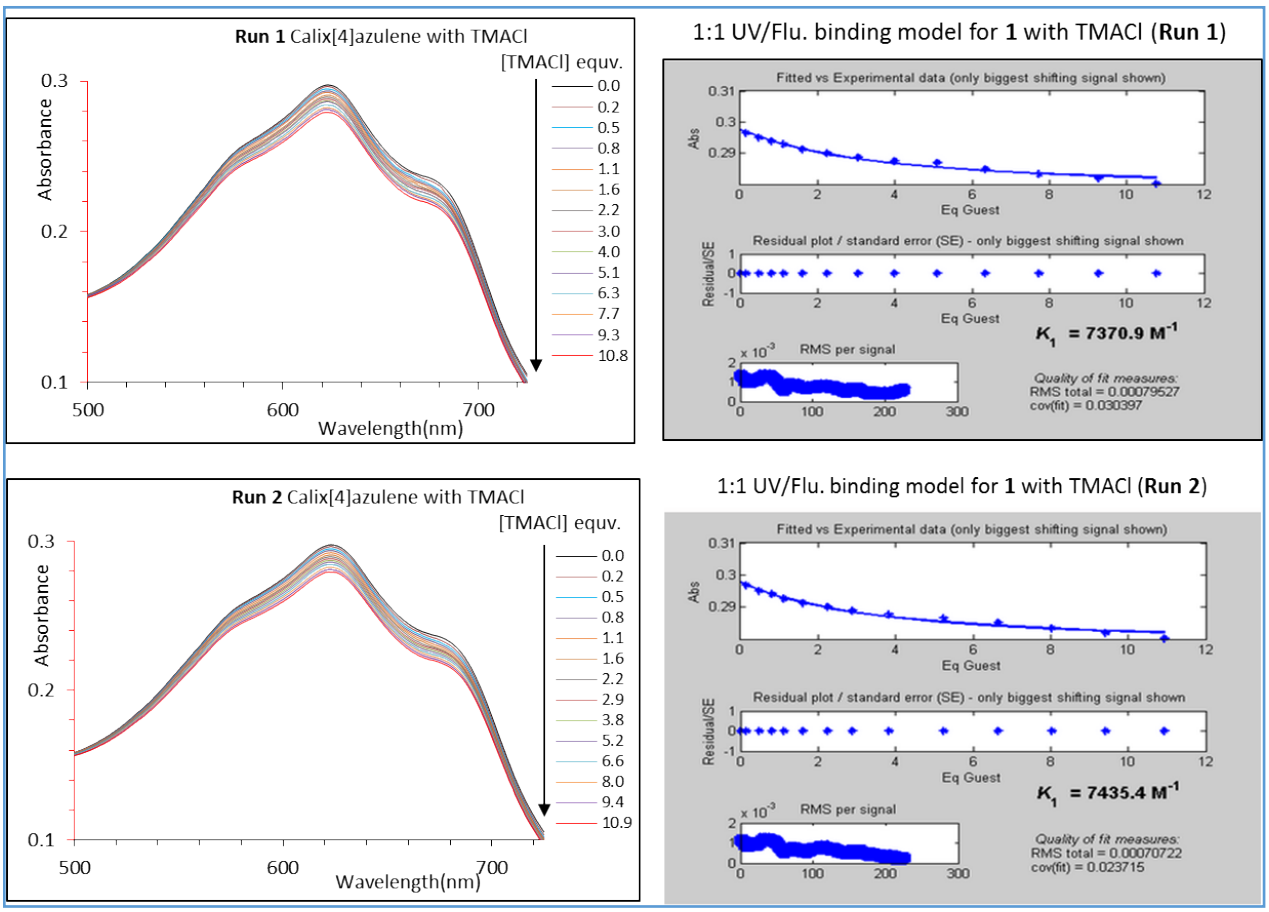

Figure S1. *Left side(Top and bottom)*: UV-vis spectra of calix[4]azulene **1** (4.82×10^{-5} M) upon addition of TMACl (0~10 equivalents) in 9:1,v/v CH_3Cl/CH_3OH and *Right side(Top and bottom)*: Screenshot (www.supramol.com) showing 1:1 binding model for calix[4]azulene **1** with TMACl.

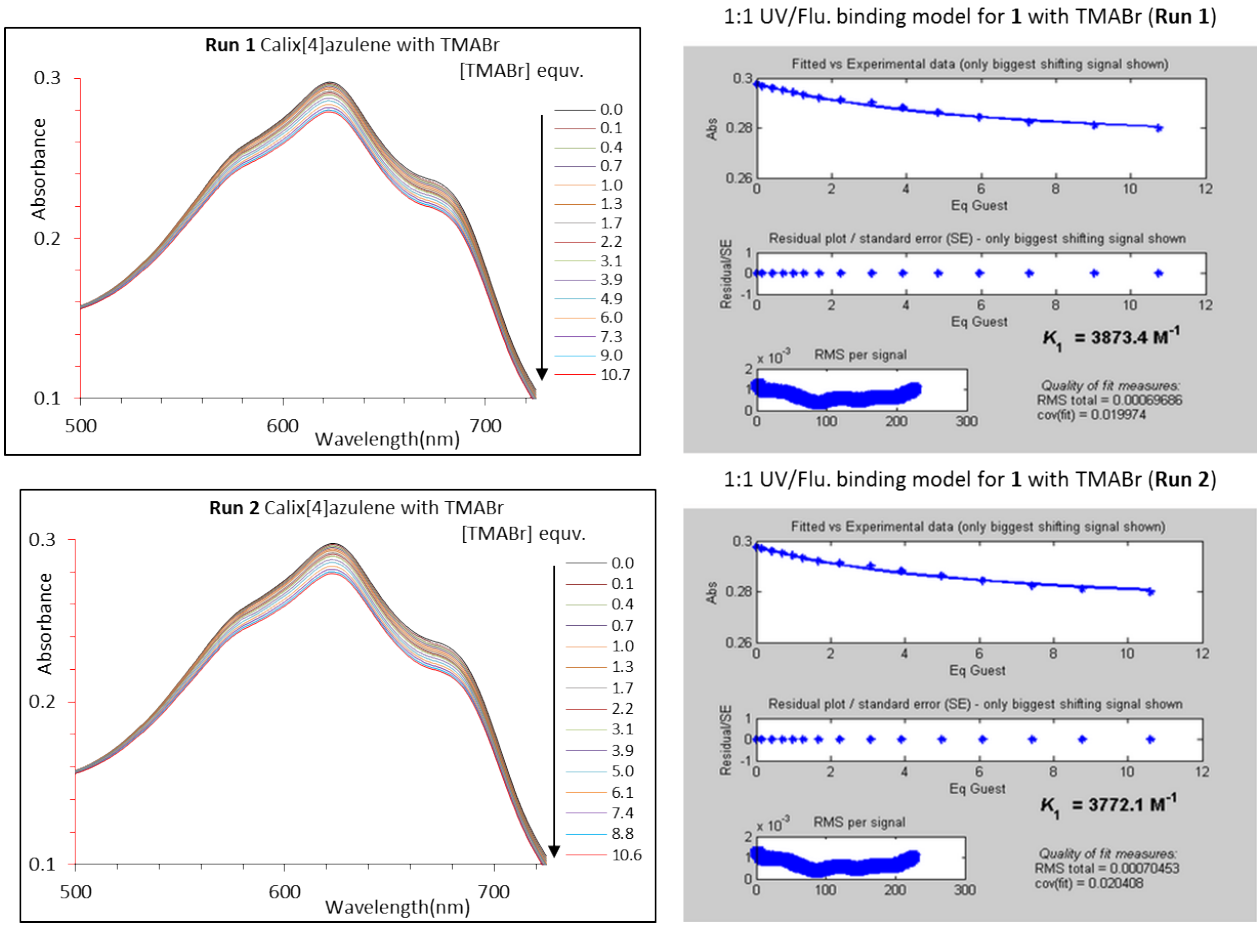

Figure S2. *Left side(Top and bottom)*: UV-vis spectra of calix[4]azulene **1** (4.82×10^{-5} M) upon addition of TMABr (0~10 equivalents) in 9:1,v/v CH_3Cl/CH_3OH and *Right side(Top and bottom)*: Screenshot (www.supramol.com) showing 1:1 binding model for calix[4]azulene **1** with TMABr.

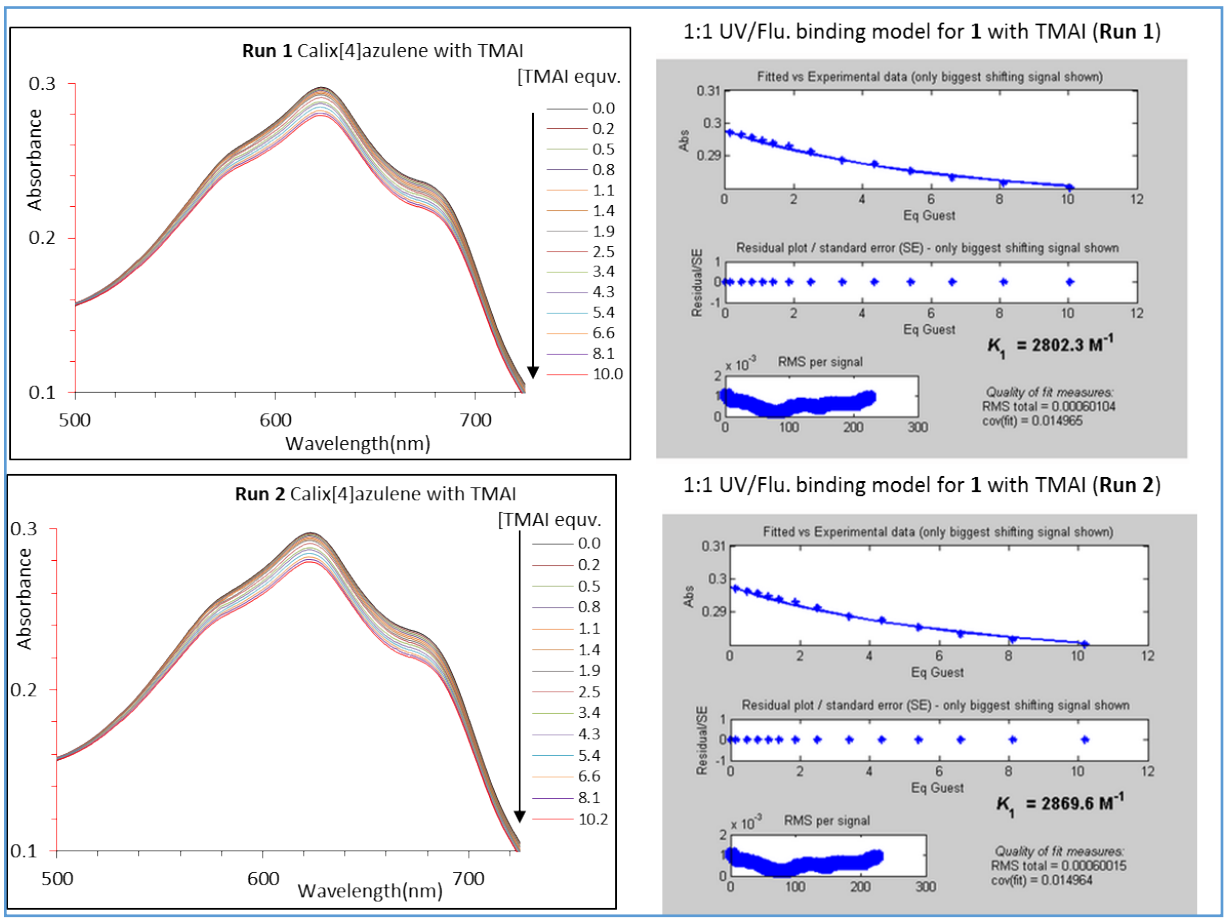

Figure S3. *Left side(Top and bottom)*: UV-vis spectra of calix[4]azulene **1** (4.82×10^{-5} M) upon addition of TMAI (0~10 equivalents) in 9:1,v/v CH_3Cl/CH_3OH and *Right side(Top and bottom)*: Screenshot (www.supramol.com) showing 1:1 binding model for calix[4]azulene **1** with TMAI.

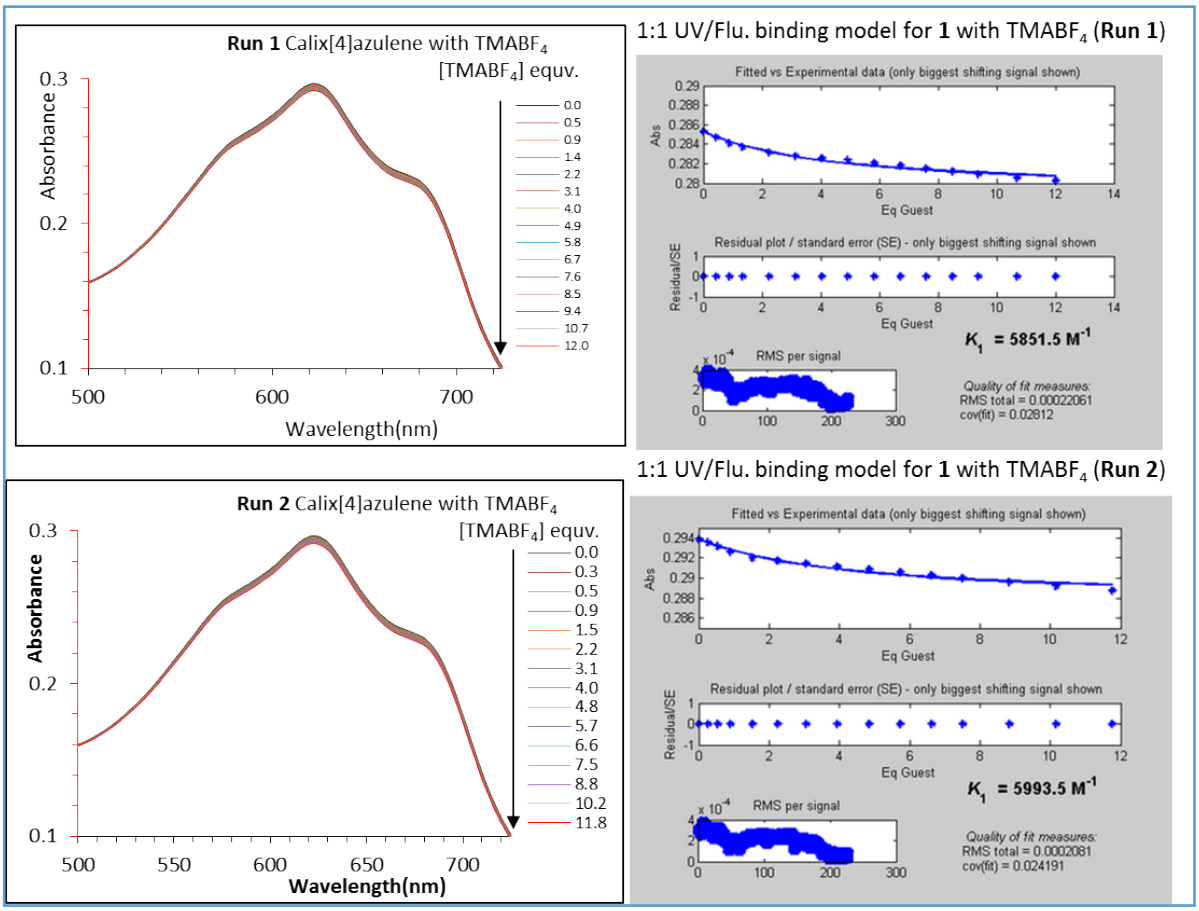

Figure S4. *Left side(Top and bottom)*: UV-vis spectra of calix[4]azulene **1** (4.82×10^{-5} M) upon addition of $TMABF_4$ (0~10 equivalents) in 9:1,v/v CH_3Cl/CH_3OH and *Right side(Top and bottom)*: Screenshot (www.supramol.com) showing 1:1 binding model for calix[4]azulene **1** with $TMABF_4$.

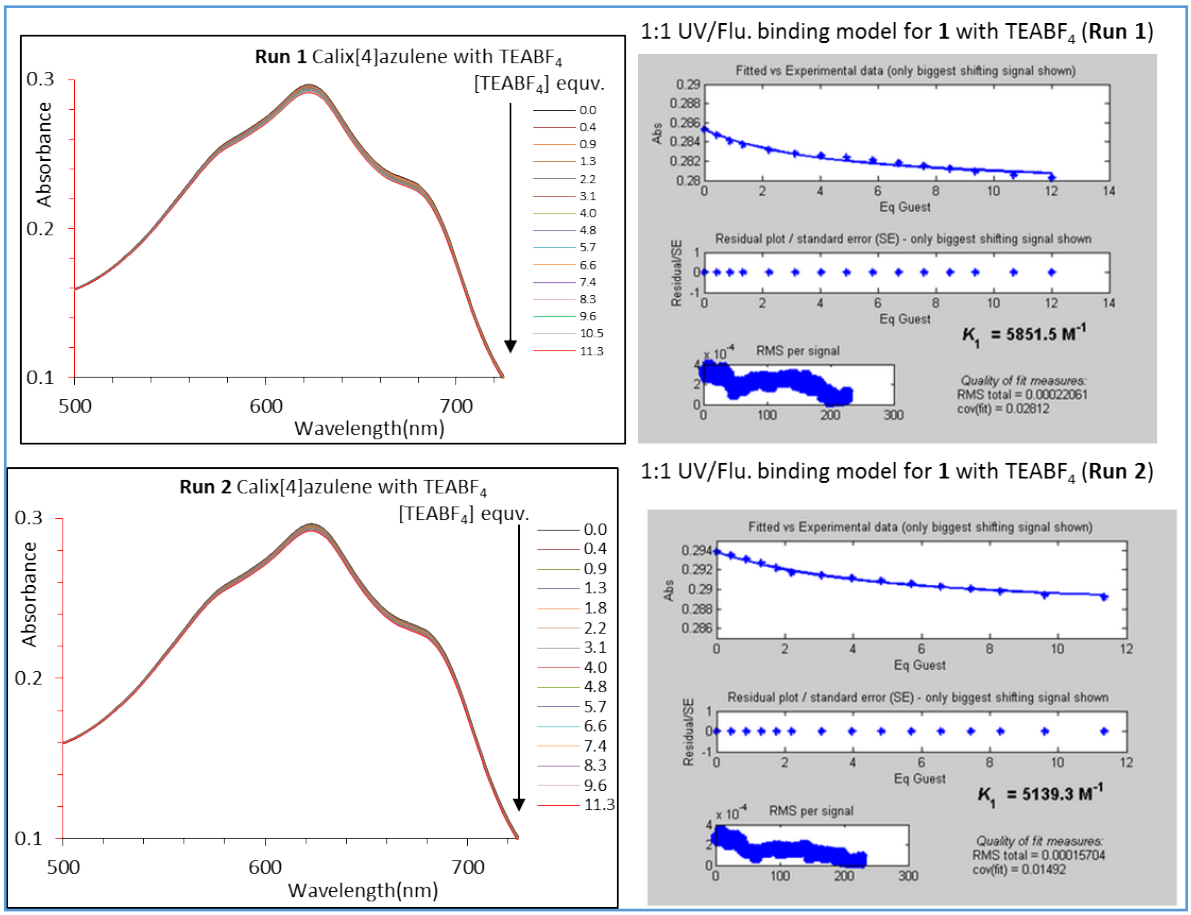

Figure S5. *Left side(Top and bottom)*: UV-vis spectra of calix[4]azulene **1** (4.82×10^{-5} M) upon addition of $TEABF_4$ (0~10 equivalents) in 9:1,v/v CH_3Cl/CH_3OH and *Right side(Top and bottom)*: Screenshot (www.supramol.com) showing 1:1 binding model for calix[4]azulene **1** with $TEABF_4$.

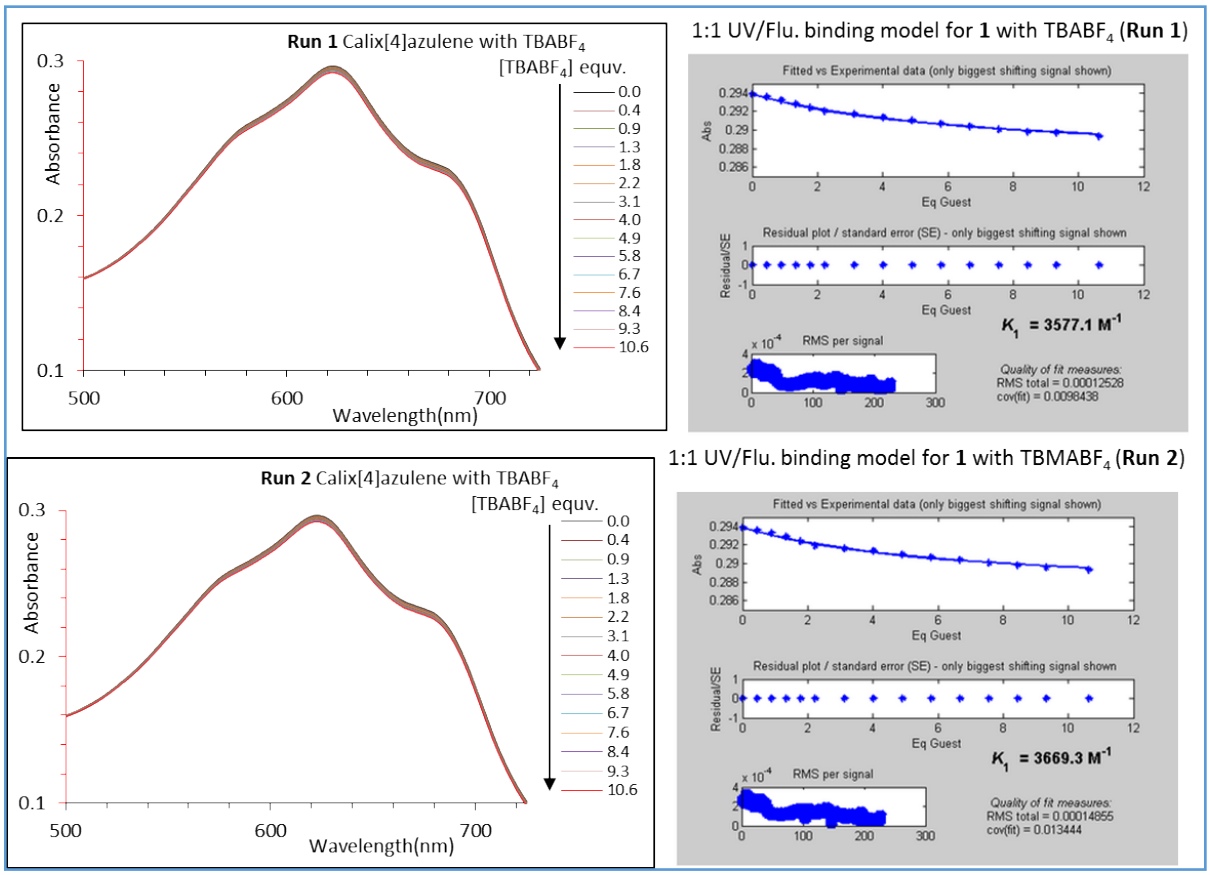

Figure S6. *Left side(Top and bottom)*: UV-vis spectra of calix[4]azulene **1** (4.82×10^{-5} M) upon addition of $TBABF_4$ (0~10 equivalents) in 9:1,v/v CH_3Cl/CH_3OH and *Right side(Top and bottom)*: Screenshot (www.supramol.com) showing 1:1 binding model for **1** calix[4]azulene **1** with $TBABF_4$.

References

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr. J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.: Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision D.01*; Gaussian, Inc., Wallingford CT, 2013.
2. (a) P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305-1323; (b) www.supramol.com.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shelxl

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: shelxl

```
Bond precision:  C-C = 0.0030 A          Wavelength=0.71075

Cell:            a=21.779(11)     b=4.904(2)         c=27.269(12)
                 alpha=90         beta=97.075(8)     gamma=90
Temperature:     153 K

                 Calculated                Reported
Volume           2890(2)                   2891(2)
Space group      C 2/c                     C 1 2/c 1
Hall group       -C 2yc                    -C 2yc
Moiety formula   C44 H32                   C44 H32
Sum formula      C44 H32                   C44 H32
Mr               560.70                    560.69
Dx,g cm-3        1.289                     1.288
Z                4                         4
Mu (mm-1)        0.073                     0.073
F000             1184.0                    1184.0
F000'            1184.43
h,k,lmax         26,6,34                   26,6,34
Nref             2988                      2982
Tmin,Tmax        0.989,0.997               0.985,0.998
Tmin'            0.976

Correction method= # Reported T Limits: Tmin=0.985 Tmax=0.998
AbsCorr = NUMERICAL

Data completeness= 0.998          Theta(max)= 26.492

R(reflections)= 0.0658( 2647)     wR2(reflections)= 0.1415( 2982)

S = 1.179                 Npar= 200
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT031_ALERT_4_C Refined Extinction Parameter within Range ..... 2.667 Sigma

Author Response: Refining the extinction parameter yielded slightly better refinement values, and so it was included with its standard uncertainty.

PLAT906_ALERT_3_C Large K value in the Analysis of Variance ..... 13.349 Check

Author Response: The large value of K was for Fc/Fc(max) = 0.007. All others were between 0.871 and 1.866.

PLAT906_ALERT_3_C Large K value in the Analysis of Variance ..... 2.098 Check

Author Response: The large value of K was for Fc/Fc(max) = 0.007. All others were between 0.871 and 1.866.

PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 2 Report

Author Response: These may have been obscured by the beamstop.

Alert level G

PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical ? Check
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Th(Min) ... 3 Report
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 2 Note

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
3 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 29/01/2015; check.def file version of 29/01/2015

Datablock shelxl - ellipsoid plot